ALAGAPPA UNIVERSITY

[Accredited with 'A+' Grade by NAAC (CGPA:3.64) in the Third Cycle
and Graded as Category–I University by MHRD-UGC]
(A State University Established by the Government of Tamilnadu)

KARAIKUDI – 630 003

DIRECTORATE OF DISTANCE EDUCATION

M. Sc.,

IV - SEMESTER

34442

APPLIED CHEMISTRY

SYLLABI-BOOK MAPPING TABLE

APPLIED CHEMISTRY

Syllabi	Mapping in Book
Unit-1 : Environmental Chemistry Hazardours materials and their ill effects. Acid rain, ozone hole and green house effect. Types of pollution-air, water,land,pesticide,thermal and radioactive. Physicochemical and biological investigations of water- water quality	**Pages 1 - 30**
Unit-2: Wastewater treatment methods Pretreatment, preliminary treatment, secondary(or biological) methods of treatment and tertiary(or advance) methods of wastewater treatment.	**Pages 31 - 38**
Unit -3: Electrochemical power sources Principle of energy conversion, electrochemical energy conversion, Classification of batteries-primary and secondary systems. Basic electrochemical reactions and performance of primary and secondary systems-Fuel cells-Introduction-Types of fuel cells, Advantages –fuel cell, supercapcitors	**Pages 39- 50**
Unit-4:Corrosion Basic aspects of corrosion: Importance of corrosion studies-EMF and Galvanic series-classification of corrosion-corrosion kinetics-Pourbaix diagram for Fe-H_2O sytem-passivity	**Pages 51 – 67**
Unit-5 Methods of Corrosion High temperature corrosion-Forms of corrosion. Chemical and Electrochmeical methods of corrosion rate measurements methods	**Pages 68 - 92**
Unit -6 : Corrosion control methods General classification of corrosion control methods-Designing aspects in corrosion control-corrosion inhibitors-Electrochemical methods of protection such as anodic and cathodic protection	**Pages 93 -110**
Unit-7: Electroplating Principles of electroplating-Metal deposition form solutions of simple salts and complex salts-measurement of current density, throwing power and current efficiency of electroplating bath-surface preparation for electroplating. Electroplating of nickel and copper.	**Pages 111- 119**

CONTENTS

Course Material Prepared by
Dr. A.N. Senthilkumar
Assistant Professor
PG & Research Department of Chemistry
Alagappa Govt. Arts College, Karaikudi -3.

Course Material Reviewed by
Dr. N. Sengottuvelan
Assistant Professor
Directorate of Distance Education
Department of Industrial Chemistry
Alagappa University, Karaikudi -3

BLOCK – I:

Environmental Waste Water Treatment Methods and Electro Chemical Power Sources

Unit-1: Environmental Chemistry

Structure

1.0 Introduction

Our environment is a complex dynamic system in which all forms of life are inter-connected and encompasses various non-stop self-generating cycles. For example green plants photosynthetic activities

NOTES

consume carbon dioxide and provide oxygen to man and other animals. Plants and micro-organisms provide pure water in lakes and rivers. Biological processes, that have gone in the soils for thousands years provide coal, petroleum, food, etc. Rapid industrialization and modernization of human life styles have violated nature's law and broken the cycles. As a consequence, the air we breathe, the water we drink, and the places where we live and work are contaminated with toxic substances. Similarly the quantum of effluent discharged from the industries is quiet high which in turn drives crucially for water treatment before discharge into water bodies.

1.1 Objectives

After going through this unit you are able to

- Understand the environmental toxicity noticed around us
- Appreciate the various by which our environment is polluted
- Acquire knowledge about the quality of water

1.2 Hazardous Materials and Their Ill Effects

Hazardous material is a common term constituting hazardous, chemical, infectious and medical wastes which are potentially harmful to human health and environment. A hazardous material is a substance or mixture of substances having properties capable of producing adverse effects on the health and safety. Hazardous materials include solid waste, hazardous substances, hazardous waste, hazardous chemicals and medical waste. Hazardous materials will have the following characteristic

- Inflammable
- Corrosive
- Liberates toxic gas upon reaction
- Toxic
- Medical waste

The following are the comprehensive list of toxic chemicals causing human hazards

NOTES

Eight elements or ions	Thirty-one organic substances	
Arsenic (As)	benzene	hexachloroethane
Barium (Ba)	carbon tetrachloride	lindane
Cadmium (Cd)	chlordane	methoxychlor
Chromium (Cr)	chlorobenzene	methyl ethyl ketone
Lead (Pb)	chloroform	nitrobenzene
Mercury (Hg)	o-cresol	pentachlorophenol
Selenium (Se)	m-cresol	pyridine
Silver (Ag), and	p-cresol	tetrachloroethylene
	1,4-dichlorobenzene	toxaphene
	1,2-dichloroethylene	trichloroethylene
	1,1-dichloroethylene	2,4,5-trichlorophenol
	2,4-dinitrotoluene	2,4,6-trichlorophenol
	endrin	vinyl chloride
	heptachlor	2,4-D
	hexachlorobenzene	2,4,5-TP silvex
	hexachloro-1,3-butadiene	

Table 1.1 List of notified hazardous chemicals

Toxic substances can enter our bodies using the following four ways.

- Absorption
- Ingestion
- Injection
- Inhalation

Absorption of toxic substance through the skin or eye could cause mild irritation or acute problems like burns, sores, or ulcers on the outer layers of the skin. Extent of contamination is based on hazardous substance and the condition of the skin. Eyes are particularly sensitive to toxic substances and the substance can enter the bloodstream by capillary action more readily. Eye contact with toxic substances can cause irritation, pain, or even blindness.

Injection is the most familiar way to administer medicine, in which the skin is punctured with needles so that a substance can enter the body. Injection can also occur accidentally. For example, if the skin were cut by a contaminated can or a piece of glass that had been in contact with a contaminant, the contaminated substance could be injected into the body. This is a very powerful means of exposure because the contaminant enters the bloodstream immediately.

Ingestion ingests a substance that contains a harmful material and enters the body by means of the digestive system. An example of inadvertent ingestion is a battery factory employee who eats lunch in the work area and ingests inorganic lead that has contaminated a sandwich. A more common instance is the child who puts a toxic substance in his or her mouth out of curiosity. Residue from chemicals that have been added to food to kill germs or parasites may also be ingested.

NOTES

Inhalation is also possible to be contaminated by toxic substances by breathing them into the lungs. The amount of air inhaled in a workday can be extremely large, so if an individual works or lives in a contaminated area, he or she can be exposed to significant quantities of a substance in this way.

1.2.1 Extent of Severity

Hazardous substances can cause short-term and long-term health problems, both of which have symptoms that can range from mild to severe. The milder effects include slight eye or skin irritation. More serious effects can include chronic lung disease and cancer, which are not always immediately obvious to sufferers. Gradual worsening of a serious condition or the acute exposure to a particularly dangerous substance causes brutality. The common health problems that can occur from exposure to hazardous substances are listed below

- **Dermatitis** – an itchy, inflammation of the skin caused by direct skin contact to substances.
- **Asthma** – a result of developing an allergy to substances used at work
- **Losing consciousness** – a result of being overcome by toxic fumes
- **Cancer** – likely to appear long after the exposure to the substance that caused it
- **Viral Infection** – caused by bacteria and other micro-organisms

This list is far from exhaustive. It is also important to note that different individuals may have very different reactions to the same substance. Something that has an extreme effect on one person could have no effect at all on another even if both have experienced the same or similar exposure to that substance.

1.3 Acid Rain

Various industrial and automobiles activities release huge volumes of acidic oxides such as carbon dioxide, sulphur dioxide, nitrogen dioxide, hydrogen chloride, etc., into the atmosphere. These oxides dissolve in moisture present in atmosphere to form corresponding acids, which then fall slowly on earth as acid-rain. The various chemical reactions which take place are depicted as follows

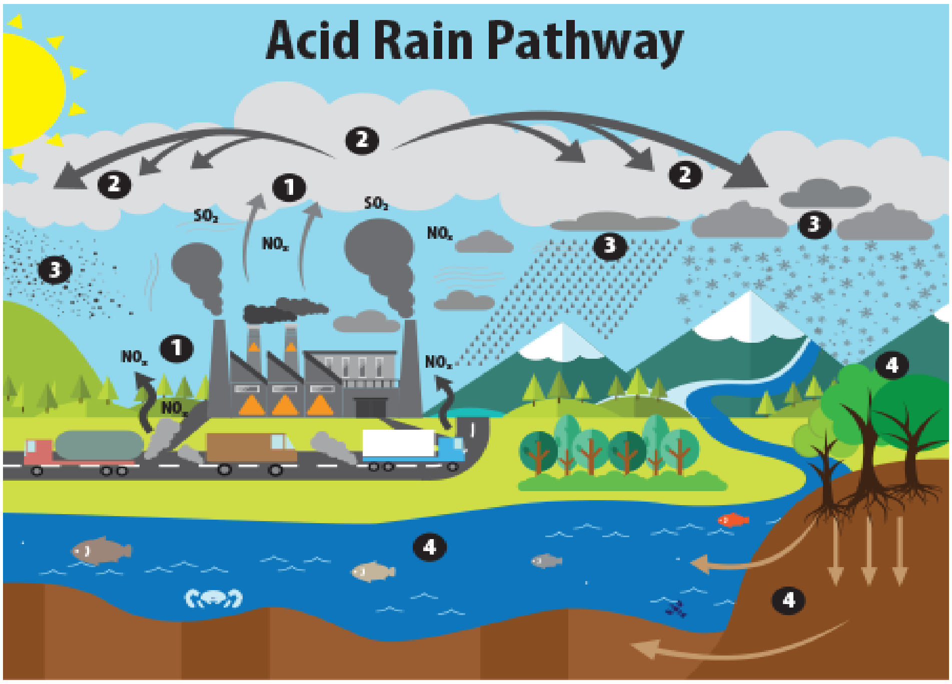
$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (Sulphurous acid)}$$

$$2\,SO_2 + O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4 \text{ (Sulphuric acid)}$$

$$4\,NO_2 + 2\,H_2O + O_2 \rightarrow 4\,HNO_3 \text{ (Nitric acid)}$$

$$HCl(g) + H_2O \rightarrow HCl\,(aq) \text{ (Hydrochloric acid)}$$

$$CO_2\ (g) + H_2O \rightarrow H_2CO_3\ (aq)\ \text{(Carbonic Acid)}$$



This image illustrates the pathway for acid rain in our environment:
(1) Emissions of SO_2 and NO_x are released into the air, where (2) the pollutants are transformed into acid particles that may be transported long distances. (3) These acid particles then fall to the earth as wet and dry deposition (dust, rain, snow, etc.) and (4) may cause harmful effects on soil, forests, streams and lakes.

Figure 1.1 Various pathways of acid rain

1.3.1 Harmful Effects of Acid-Rain

Increased extent of acid rain during the past years has progressively increased the acidity or decreased pH of rain-water. Acid rain causes damage to frosh water-life and directly damage to plant leaves. Acid rain changes the rate of metabolism of organisms. It causes irritation to eyes and muscus membrane. It accelerates the rate of corrosion of metals and causes damage to buildings, rocks, etc. It, dissolves salts in the soil and metals which pass into ponds, lakes and rivers theyby causing toxic effects to aquatic-life.

1.4 Ozone Hole

Ozone (O_3) is an allotrope of oxygen is produced in the upper layer of atmosphere from oxygen gas by the absorption of ultraviolet light.

Ultraviolet

$$3O_2(g) \quad \leftrightarrow \quad 2O_3\ (g)$$

Oxygen light Ozone

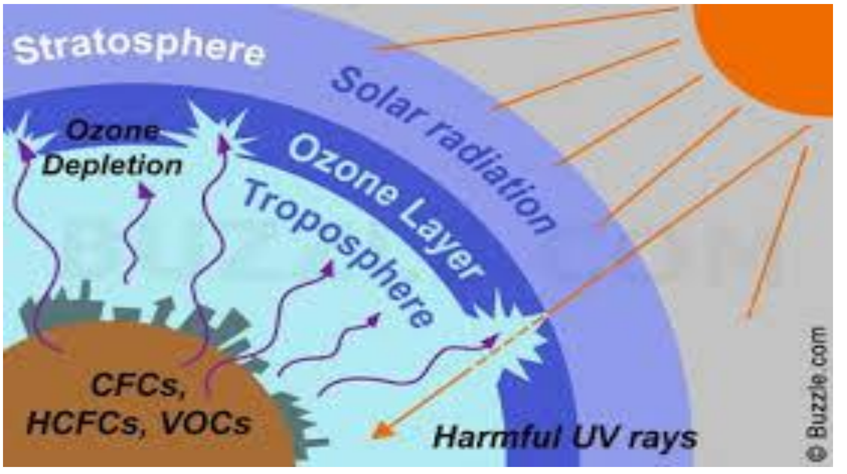


Figure 1.2 The process of ozone layer depletion

Thus, air in the upper layer is packed with higher concentration of ozone which checks the entry of ultraviolet light from sunlight. Sunlight of particular UV region would destroy many of the organic materials necessary for life. Ozone layer formation has helped the earth for its fruitful existence which sheds humankind in the present form. But the same ozone is quite destructive to fabrics, rubber goods and crops etc.

1.4.1 Importance of Ozone Layer

Ozone layer absorbs most of the harmful ultraviolet (UV) radiations coming from the sun and assist existence of life on earth. Ozone layer if depleted in the atmosphere, then the harmful UV radiations coming from the sun would reach the earth and mankind should thirst for its survival. UV radiation of particular high frequencies in the range of 200 nm would damage the plants causes diseases like skin cancer in animals and men, and can cause the slow deterioration of life on the earth.

1.4.2 Causes of Depletion of ozone layer

Chlorofluorocarbons (CFCs) are the main culprits responsible for ozone layer depletion. The exhausts of supersonic aircrafts and jumbo jets flying in the upper atmosphere discharge considerable amount of ozone in to the atmosphere. They got accumulated at higher altitudes and undergo decomposition under the influence of ultraviolet radiation and releases chlorine into the atmosphere. Each atom of chlorine so-released react with more than 10^5 molecules of ozone converting ozone into oxygen. Consequently gradual depletion of ozone layer takes place and the effective capacity of ozone layer to stop ultraviolet radiation from entering the environment diminishes.

NOTES

The typical reactions causing depletion of ozone layer by chlorofluorocarbons to areshown below

$$CFCl_3 (g) \xrightarrow{hv} CFCl_2 (g) + Cl_2 (g)$$

$$CF_2 Cl_2 (g) \rightarrow CF_2Cl (g) + Cl (g)$$

$$O_3 (g) \xrightarrow{hv} O_2 (g) + O (g)$$

$$Cl (g) + O_3 (g) \rightarrow ClO (g) + O_2 (g)$$

$$O (g) + ClO (g) \rightarrow Cl (g) + O2 (g)$$

$$Cl(g) + O_3 (g) \rightarrow ClO (g) + O_2 (g)$$

$$O (g) + O_3 (g) \rightarrow 2O_2 (g)$$ **(over all)**

Also emission of nitric oxide by high flying supersonic aircrafts is responsible for ozone depletion.

$$NO (g) + ClO (g) \rightarrow Cl (g) + NO_2 (g)$$

$$Cl (g) + O_3 (g) \rightarrow ClO (g) + O_2 (g)$$

$$NO (g) + O_3 (g) \rightarrow NO_2 (g) + O_2 (g)$$

CFC's also find applications in refregeration, air-conditioning, aerosols, sterilzation, cleaning foams, etc. Thus, chlorine atoms so-produced during above two types of ozone depletion reactions cause a chain reaction. Actually, more than 10^5 molecules of ozone are converted into oxygen molecule by a single chlorine atom.

CFC	**Uses**
Freon-11 (CCl_3F)	Refrigeration, aerosol-propellants, cleaning foams, air-conditioning.
Freon-12 (CCl_2F_2)	Refrigeration, aerosol-propellants, cleaning foams, air-conditioning.
Freon-22 ($CHClF_2$)	Aerosol-propellant, cleaning solvent.
Freon-113 ($CCl_2F.CClF_2$)	Refrigeration, cleaning foams.
Freon-114 ($CClF_2$. $CClF_2$)	Refrigeration, aerosols-propellants, cleaning foams.
Freon-115 ($CClF_2$. CF_3	

NOTES

Halon-1211 (CF_2 BrCl) Halon-1301 (CF_3 Br) Halon-2402 ($C_2F_4Br_2$)	Refrigeration, air-conditioning, foams. Fire-extinguisher. Fire-extinguisher. Fire-extinguisher.

Table 1.2 CFCs and their uses.

1.4.3 Effects of Ozone Layer Depletion

Depletion of ozone layerdoes the penetration of UV radiation on earth's surface increases and causing harm to mankind. They cause skin cancer, swelling of skin, sun burns, burning sensation, skin aging, leukamia, breast cancer, cataracts of eyes, edema, haemorrhage, lungs injury, lung cancer, dizziness, visual impairment, permature aging, DNA breakage, inhibition and alteration of DNA's replication and formation of DNA adduct and finally even lead to death. The lethal dosages and their ill efects are tabulated as follows

Concentration (ppm)	**Ill effects on human health**
0.25	Admissible range
0.31	Irritation of nose and throat
0.85	Lungs undergo genetic alteration within a week.
1.1-3.2	Extreme fatique
9.4-10.0	Chronic pulmonary disorder

Table 1.3 Ill effect of ozone on human-beings.

1.4.4 Need for substitutes

Hazardous nature of CFCs screws alternatives for CFCs. Montreal protocol which is a joint agreement between 80 countries including India came with following conclusions

(i) Phase out production and consumption of CFCs not later than 2010.

(ii) Phase out production and consumption of halons as soon as possible.

(ii) Commit themselves to accelerate development of environmentally acceptable alternative chemicals in place of CFCs.

NOTES

(iv) Make available the relevant scientific informations, result and training relating to substitutes for CFCs to developing and underdeveloped countries.

1.4.4.1 Substitutes for CFCs:

On the basis of environmental impacts, hydrochlorofluorocarbons (HCFCs) and hydro fluorocarbons (HFCs) are now considered as short term ozone friendly substitutes for CFC's in the air-conditioning and refrigeration industry.

1.5 Greenhouse effect

The greenhouse effect is the natural warming of the earth by gases present in the atmosphere which trap heat from the sun. The absorbed heat present in the green houses gases is then radiated back to the earth causing warming. The main gases responsible for the greenhouse effect include carbon dioxide, methane, nitrous oxide, water vapour and fluorinated gases. Greenhouse gases have different chemical properties and are removed from the atmosphere over time by different processes. The effectiveness of green house gases in holding heat is measured as global warming potential **(**GWP) which is a measure of the total energy that a gas absorbs over a given period of time relative to the emissions of 1 ton of carbon dioxide.

1.5.1 Greenhouse Gases

Industrial revolution and over exploitation of carbon mineral for power generation increases the volume of greenhouse gases emitted into the atmosphere. CO_2 gas in the atmosphere perform major role of heating up of the atmosphere, due to trapping of infrared rays from the sun. The sun-rays consists of UV, visible, and infrared radiations. The ozone layer present in the upper atmosphere absorbs most of the UV radiation and allows visible and infrared radiations to pass through towards the earth. These infrared rays cause heating effect to the objects on the earth and atmosphere. Human activities discharges huge volume CO_2 into the atmosphere which results in additional heating of the earth environment than expected. Hence the temperature of the earth's atmosphere rises gradually. Every year the world-wide concentration of CO_2 is increasing of a rate of 0.82 ppm and the temperature is rising at a rate 0.06°C per year. Greenhouse effect ultimately melts the glaciers, polar ice caps and result in flooding of many low lying areas.

NOTES

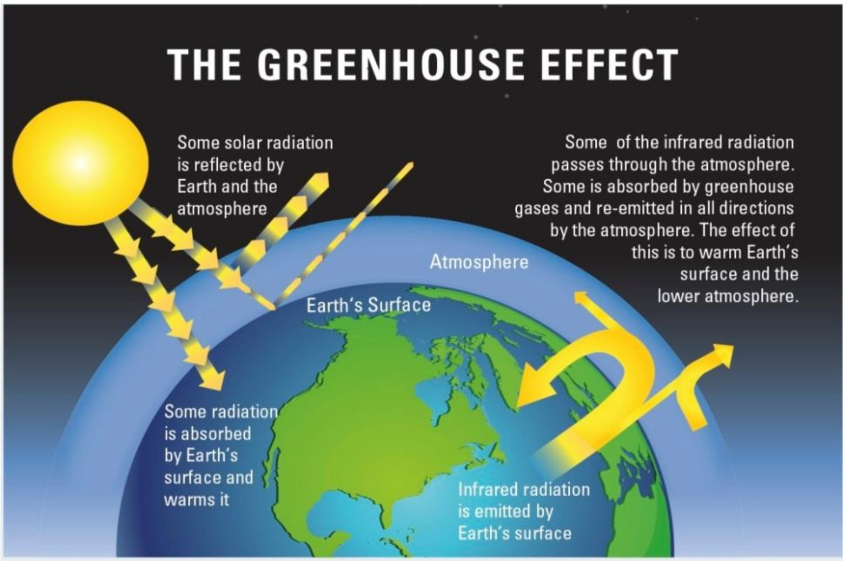


Figure 1.3 Greenhouse Phenomena

1.6 Types of Pollution

Pollution is an unwanted phenomenon which degrades the all form of environment. The particle responsible for the event is called as pollutant. The pollution process are classified into

- Air pollution
- Water pollution
- Land pollution
- Pesticide pollution
- Thermal pollution
- Radioactive pollution

1.6.1 Air Pollution

Air pollution may be defined as the excessive discharge of undesirable foreign substances into the atmospheric air thereby adversely affecting the quality of air and causing damage to human, plants and animal lives. The air pollution concerns mainly in the troposphere. The average composition of clean dry-air near sea-level is N_2= 78.09; O_2 = 20.94; Ar = 0.9; CO_2 = 0.0318; Ne = 0.018 and rest of other gases. Addition of unwanted particles to the said cleanliness induces air pollution.

NOTES

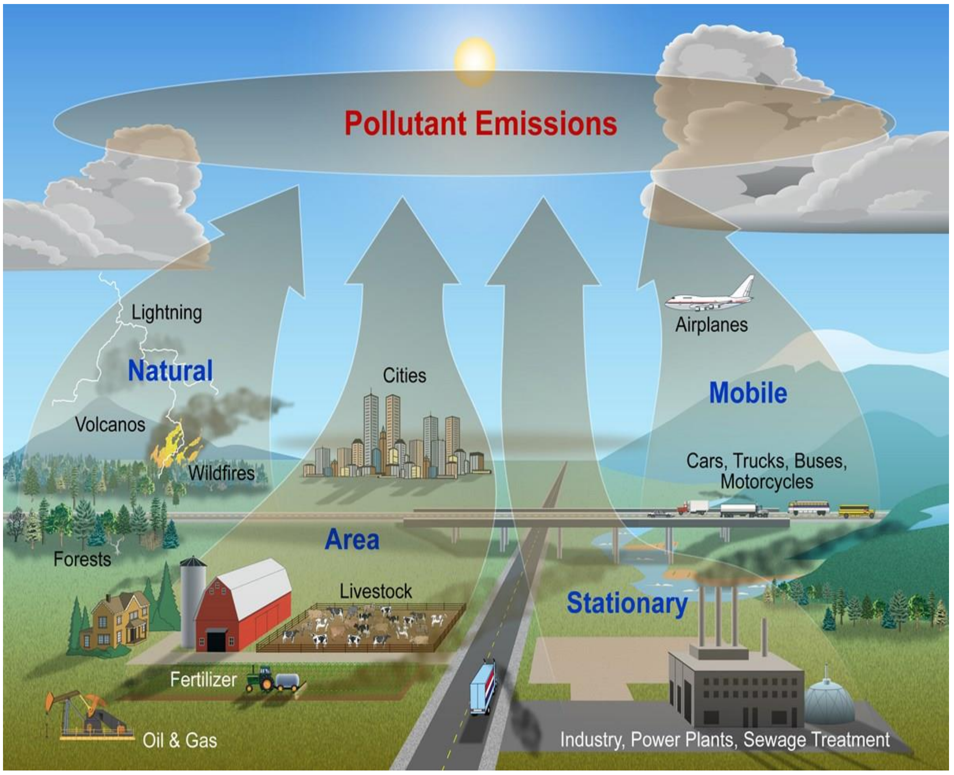


Figure 1.4 Air Pollution

1.6.1.1 Various Types of Air Pollutants

(i) **Sulphur dioxide (SO_2)** enters from thermal power plants, petroleum industry, oil refineries, sulphuric acid plants, and sulphide ore roasting plants. The presence of this gas in the atmosphere causes cardiac (heart), respiratory (or pulmonary) diseases to man (e.g., asthma, bronchitis), damages to agriculture, eye-irritation, throat troubles, besides corrosion of metals. Some effects of SO_2 in atmosphere on plants cells are membrane damage, chlorophyll destruction, metabolism inhibition, growth-yield reduction, etc.

(ii) **Sulphur trioxide (SO_3)** is formed by the oxidation of sulphur dioxide under the influence of sunlight. Even 1 ppm of SO_3 in air causes severe breathing discomfort and irritation to the respiratory tract. Presence of SO_2 and SO_3 is destructive to vegetation.

(iii) **Hydrogen sulphide** enters the atmosphere as the pollutant through the decomposition of sewage wastes or organic matter, and from various industries. It is more poisonous than even carbon monoxide and blackens lead paints and causes corrosion of metals.

(iv) **Nitrogen oxides** (like NO, NO_2) are produced from the combustion of fuels. Other sources are acid manufacture, explosive

NOTES

industry, and acid-pickling plants. Because of continuous increase in the number of vehicles, power plants, industries, etc., the pollution due to nitrogen oxides is increasing day-by-day. In high NO_2 areas, respiratory illness, among children, have been reported. It is unpleasant in odour and leads to irritation of eyes and even lung's congestion. In sunlight, nitrogen oxides and hydrocarbons (from combustion of petroleum products) form smong, which limits the visibility of roads, eye irritation and bronchitis.

(v) **Carbon monoxide (CO)** is released by the partial combustion of fuel in automobiles, industries and oil-refineries. Cigarette and bidi smoke and domestic heat-appliances are the other sources of CO. It is very toxic in nature and causes headache, visual difficulty, paralysis and even death in the human-beings. Carbon monoxide reacts with the red pigment (haemoglobin) to form carboxy-haemoglobin, thereby impairing oxygen-carrying capacity of blood leading to laziness, exhaustion of body, headache, decrease in visual perception, and serious effects on the cardio-vascular system. Prolonged exposure can even lead to death. coalso affects the cardio-vascular system, thereby causing heart diseases.

$$\underset{\text{Haemoglobin}}{Hb} + \underset{\text{(Inhaled oxygen)}}{O_2} \rightarrow \underset{\text{Oxyhaemoglobin (in tissues)}}{HbO_2} \rightarrow Hb + O_2$$

$$Hb + CO \rightarrow \underset{\text{Carboxyhaemoglobin (cannot take } O_2 \text{ from lungs)}}{HbCO} \rightarrow \text{oxygen starvation}$$

(vi) **Carbon dioxide** is released into the atmosphere in the form of smoke, which is produced by burning of fuels such as coal, wood, petroleum products, and gaseous fuels. The CO_2 is also released into air by the respiration of plants and animals. Increasing population in causing faster increase in concentration of CO_2 in the atmosphere. The concentration of CO_2, is also increased by deforestation. The plants use CO_2 for photosynthesis and release oxygen. The cutting down of forests makes the environment unhealthy by the decreasing concentration of oxygen. The excess of CO, in the atmosphere causes respiratory disorders and suffocation.

(vii) **Hydrogen fluoride** is discharged from phosphate fertilizer industry, aluminium industry, metallurgical processes, brick-kilns, pottery kilns, and coal-burnin, industries. This gas causes irritation, bone, tooth skeleton disorders and respiratory diseases.

NOTES

viii) **Aerosols** are certain chemicals released into the atmosphere with force in the form of a mist or vapour. An important source of aerosols in the upper atmosphere is the jet and aeroplane emissions. The aerosols contain fluorocarbons, used as propellants in jet engines. Aerosols from supersonic aeroplanes contain NO_2 and SO_2. Aerosols containing fluorocarbons, NO_2 or SO_2 reach within the ozone layer in the stratosphere, there by depleting ozone concentration. This allows some of the more harmful ultraviolet radiation from the sun to reach the earth's surface. Aerosols, thus dilutes the preventive shield of ozone against entry of ultraviolet light.

(x) **Photochemical oxidants :** In presence of sunlight, different unburnt hydrocarbons (released as combustion products of automobiles) react with oxides of nitrogen to form peroxyacetyl nitrates [PAN] and other complex products. Some of these photochemical oxidation products have bad effects on respiratory system and the asthetic performance of humans. They cause irritation of eyes, nose, throat, increased chances of asthamatic attack and mortality. They destroy vegetation and rubber products (e.g., tyres, insulating wires, etc.). They also form smog (a combination of smoke and fog), which causes poor atmospheric visibility.

(xi) **Hydrocarbons :** High concentration of hydrocarbons effects lungs and cause swelling when they enter the lungs. Inhalation of aromatic hydrocarbons vapours cause greater ill effects like irritation to mucus membrane, respiratory problems, lungs cancer, affect nervous system and may even lead to death. Organic compounds which induce cancer, affect DNA and cell growth, are known as carcinogens.

1.6.1.2 Particulates

Dust from mines and quarries, furnaces, power houses, vehicular traffics, house cleaning dusts, pottery and ceramics factory stacks, agriculture, forest fires, natural winds etc. Dust causes allergic and respiratory diseases, silicosis, if dust contains silica. Dust also causes corrosion and soiling. Smoke composed of tiny particles of carbon, ash, oil, etc. is invariably formed by incomplete combustion of fuel. The major sources of smoke emission are rails, roads, locomotives, domestic wood, coal-grates, industrial power plants, open fires etc. causing loss of fuel value, spoiling of clothings, rags and exterior finish of buildings. The incidence of cancer is being increasingly related with smoke. Smog is a mixture of smoke from coal combustion and fog in suspended droplet form. The two types of smog are London smog and Los Angles smog causing irritation to eyes and lungs, may damage plants, irritation to nose, throat and increased chances of asthamatic attack. Asbestos widely

used in industry for its mechanical strength and resistance to heat especially as thermal insulation material and in high temperature applications, where the high chemical stability of the silicate structure serves well. Tiny asbestos fibres readily penetrate the lung tissues and the digestive tract, and they remain there over a long period of time. Lead is known to be toxic to human metabolism but, still it is widely used in our society. The toxic effects of lead on humans are cumulative. It enters the body either as inorganic lead (Pb^{2+}) ion or as tetraethyl lead.

Tetraethyl lead is even more poisonous than Pb^{2+}. Lead also the affects the central nervous system and impairs kidney functions. The toxicity of mercury depends very much depends on it state. Pure mercury is not particularly poisonous; in fact, ingestion of a very smal1 amount of mercury (e.g., from the dental amalgam) produces no noticeable ill effects, since the metal apparently passes through the body without undergoing chemical change. On the other hand, mercury vapour is very dangerous, because it causes irritation and destruction of lung tissues. Mercury in vapour form adversely effect the neurological behaviour of humans. Cadmium is the waste product from industrial processes. It is toxic to living organisms, even in low concentration of loss than 1 mg/L.

1.6.1.3 Deforestation

Green plants (leaves) use CO_2 for the manufacture of food by photosynthesis and give out O_2, thereby purifying the atmospheric air. Plants also control hydrogen sulphide, nitric acid and chlorine. Thus, plants help in controlling the air pollution. Excessive cutting of trees, consequently, causes indirectly air pollution.

1.6.1.4 Control of Air Pollution

The best way to control air pollution is to reduce or prevent the formation of pollutant at the source itself. Some of our industrial processes may be suitably modified so as to minimize the extent of pollution. Various air pollution control methods are:

(i) Emissions from automobiles and vehicles may be minimized by cleaning the exhaust gases after combustion, through the use of catalysts.

(ii) The use of tall stacks or chimney" reduces substantially the concentration of air pollutants at the ground level. The gases discharged, through stacks get diluted and are dispersed into the atmosphere.

(iii) Cyclone collector are used as precleaner of air which operates on the principle that particulates present in a gaseous stream possess greater inertia than the gas molecules. In this method, gas

containing particulates is allowed to flow into a tight circular spiral-fitted chamber. The centrifugal force exerts great inertial effect on the dispersed particulates, thereby forcing the particulates to move away from the gas and towards the walls of the chamber, from where they start settling down due to force of gravity. The particulates so-collected at the bottom of the chamber are removed periodically.

(iv) Growing more trees use carbon dioxide for their food by photosynthesis and release oxygen in the air. Consequently, they help to reduce the excess carbon dioxide of the environment. Many plants also absorb and remove significant amounts of hydrogen sulphide and nitric acid.

1.6.2 Water Pollution

The water pollution is defined the contamination of water by pollutant and lower its water quality index thereby making unfit any function and purposes. It can be defined as any alteration in the physical. chemical and biological properties of water by contamination with foreign substance which would cause a health hazard or reducing its utility.

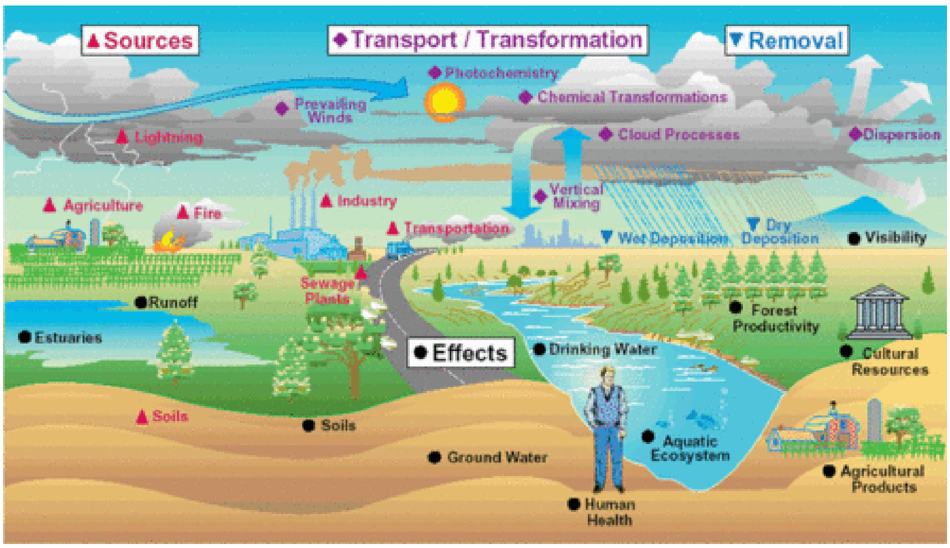


Figure 1.5 Water Pollution

1.6.2.1 Sources of water pollution

(1) Domestic sewage:

The sewage is a combination of human faces, urine, kitchen wastes, street wastes, and organic substances that provide nutrition for bacteria’s and fungi. The release of huge quantities of municipal wastes into the canals and rivers causes pollution of water bodies. Disposal of

NOTES

sewage into rivers and lakes causes the spread of water-borne diseases like dysentery, cholera, typhoid), hookworm infections, entroviral infections, and malaria.

(2) Industrial waters

Water get polluted by the effluent discharge from chemical industries such as acids, alkalis, detergents, soaps, phenols, cyanides, copper, zinc, lead, mercury, pesticides, insecticides and fungicides, etc. Pollution is also caused by wastes of industries like leather tanneries, sugar, paper, breweries, slaughter houses, textile, steel mills, soap, distilleries, oil refineries, pharmaceuticals, etc. Water containing toxic substances damage the biological activity and kills useful organisms.

(3) Fertilizer Impact

Fertilizers lead to accumulation of nitrates in water and when such water used by human-beings they are reduced to nitrites which can causing serious suffocation and injuring to respiratory and vascular system. Excessive addition of nitrates and phosphates (from agricultural waste water) into aquatic system, causes 'eutrophication', which leads to depletion of oxygen in water (due to excessive growth of algae), thereby BOD of water in increased. This leads to death of fish and other aquatic life.By bacteria, viruses, algae and diatoms (like protozoa): These cause bacterial pollution, which is due to the presence of mammals like dead bodies of man, wild and domestic animals, birds etc. in water bodies. They degrade the quality of water, Such contaminated water supplies frequently create infections like dysentry, cholera, typhoid, gastroenteritis, infectious hepatitis, polio, etc. By run-off from urban areas : Effluents from urban areas containing substances like oils, greases detergents, nutrients, heavy metals, etc. Of these, the biggest contribution to water pollution is industrial wastes and next comes sewage (street washing, urine, kitchen wastes, human excreta, etc.).

(4) Other sources

Residual pesticides, fungicides, insecticides, etc. present in the land forms are washed down into river, lakes etc., and pollute them. The surface water, sometimes, contains a high concentration of suspended solids organic as well as inorganic, bacterias, viruses, protozoa, algae, etc. This makes water unfit for domestic as well as industrial purposes. Oil from oil spills and washing of automobile pollutes our rivers. Wastes like acid-wash, alkali-wash, cyanides, phenols, mercury from paper industries, lead, zinc, copper, etc. are released into water sources, and they all cause water pollution. Atomic explosion and processing of radioactive materials, near the sources of water, cause water pollution.

NOTES

Wastes from fertilizer plants containing nitrates, phosphates, ammonia, etc., are released in water and they all cause water pollution. Clay, ores, fine particles of soil on which water travels are added to water sources and they all cause water pollution. Agricultural discharge such as pesticides, insecticides, plant nutrients, fertilizers, herbicides, manure slurry, drainage from plants and animal debris, farm wastes, etc.

1.6.2.2 Water pollution control methods:

The problem of water pollution can be reduced by using the following techniques

(i) Stabilization of ecosystem by waste reduction

(ii) Recycling of the waste water by suitable treatment,

(iii) Waste-water reclamation

(iv) Use of alternative chemicals

(v) Dilution of waste waters before their discharge

(vi) Removal of pollutants techniques such as adsorption, ion-exchangers, electro dialysis, reverse osmosis, etc.

1.6.3 Soil or Land Pollution

Soil pollution is the addition of unwanted chemical substances to the soil system thereby suppressing the soil fertility. Any substance capable of changing the productive capacity of the soil is termed soil pollutant. The polluted soil produces inferior quality of crop and that too in reduced quantity. Polluted soil cannot effect the nature of the adjacent soil.

1.6.3.1 Sources of soil pollution

The chief sources of soil pollution are

- Soil-erosion, due to deforestation over-grazing, unplanned irrigation and defective
- agricultural practice.
- Pollutants present in air and fall-out from smoke stacks of chemical works.
- Disposed human and animal excreta, solid and liquid wastes.
- Domestic refuge and industrial wastes dumped on land.
- Chemicals like fertilizers, pesticides, bectricides applied to plants and soils.

NOTES

- Radioactive wastes discharged from industrial and research centres and hospitals.
- Soil gets polluted by the removal of its upper fertile layer.

1.6.3.2 Controlling of soil pollution

The soil pollution can be controlled in the following ways

The untreated waste is buried in under earth called land fills. (2) Improving forestation areas by planting tress. Avoiding the throwing away negligently solid wastes such as garbage, ash, sludge, building materials, empty bottles, etc. on the soil. Chemicals which have a relatively high immediate as well as persistent toxicity may be used in special situation only and not for general use. Industrial and sewage wastes should be property treated before disposal on land.

1.6.3.3 PESTICIDES POLLUTION

The use of pesticides is the integral part of modern crop management practices. It has been estimated that crop damage is as high as 20% where pesticides are not used. Pesticides include chemicals to protect crops from insects (insecticides), weeds (herbicides), disease causing microorganisms (fungicides and bactericides), mites (acaricides), nematodes (nematicides) and rotents (rotenticides). Pesticides also include chemicals that control pests directly hazardous to animals and humans, particularly vectors-such as mosquitoes, flies, fleas, ticks and lice that transmit diseases. Chlorine is the basis for many of the most toxic and persistent synthetic chemicals known. It tends to combine with hydrocarbons to form organochlorines, which are toxic, persistent and bioaccumulative to all living organisms. The pesticides can generally be divided as organochlorine compounds, organophosphorus compounds, organocarbonates and miscellaneous compounds. It is estimated that more than 1000 chemicals are available for being used as pesticides. Chlorine bleaching involves generation and disposal of toxic organochlorine chemicals, including dioxin. Many extremely hazardous chemicals like phosphamidon, Dichlorvos (DDV) and paraquat can also be generated. Endosulphan and DDV are listed as highly hazardous substances, because these chemicals have the potential for long range transport and entrance into the food chain. In India, 143 pesticides are registered, with an annual consumption of about 85,000 tonnes.

The harmful effects of a pesticide depend on its toxicological properties and the degree of exposure of humans to the pesticides residue. Many of these chemical are deadly not only to the intended or particular organisms, but also to other life forms, including manWhen magnification of some of the pesticides takes place biologically, the

NOTES

process is known as biological amplification. Several pesticides such as DDT and other chlorinated hydrocarbons have persistent effectiveness of their residual deposits. DDT has got half life of 10-15 years.

There are three important ways through which the general population can be exposed to pesticides. They are:

(a) Through vector control.
(b) Through residues in the environment
(c) Through residues in the food.

Some population tends to have only a lowdose, chronic exposure, but larger doses can also be transmitted, if the exposure is persistent and bioaccumulative. Persistent pesticides move through air, water and soil, finding their way into living tissues, where they can bio-accumulate up in food chain into human diets. Almost 85-90% of pesticides applied agriculturally ever reach target organisms, but they disperse through air, water and soil. People, who are expected to be exposed to high levels of bioaccumulated pesticides include:

(a) Habitual consumers of fish, livestock and dairy products.
(b) Foetuses not nursing infants whose mother's bodies have accumulated persistent pesticides, and
(c) Sick people who metabolise their fatty tissues, which contain bio-accumulated pesticides while ill.

1.6.3.4 SOURCES OF PESTICIDAL POLLUTANTS IN WATER

Pesticides may enter aquatic ecosystem either directly, indirectly or unintentionally through the following sources:

1. Rain water
2. Spray drift
3. Runoff from agricultural fields
4. Industrial effluents
5. Domestic sewage

1.6.3.5 PERSISTENT PESTICIDES

Pesticides are most widespread molecules in various segments of environment. Their impact on the environment depends on the following factors:

a) Tendency to dissolve in water
b) Tendency to vapourize and
c) Chemical stability toward degradation processes.

NOTES

Persistence of various pesticides in soil

Pesticide	Persistence in soil
Heptachlor	9 years
Aldrin	9 years
Dieldrin	9 years
DDT	10 years
BHC	11 years
Chlorodane	12 years
Diuron	19 months
Slimazine	17 months
Atrazine	18 months
Monuron	36 months
2,4-D	14-36 days

A Major concern particularly about chlorinated hydrocarbons like DDT, aldrin, heptachlor, etc. is their persistence in soil and their movement into water bodies through soil erosion and entry in the food chain of various wildlife. Their movement in soil, leaching water and absorption by plants and changes in microbial activity in soil are of great concern. Some of these pesticides are very persistent in soils. Hence they are cause of concern to human beings. Pesticides in te soil act as reservoirs from where they find their way in water bodies.

1.6.3.6 Control of Pesticidal pollution

The proper remedy for the said pollution is application of bio pest and switching of agricultural practice towards organic farming.

1.6.4 Thermal Pollution

It is the degradation of water quality by any process which changes normal water temperature. A common cause of thermal pollution is the use of water as a coolant by power plants and industries.

1.6.4.1 Causes of Thermal Pollution

The following are the factors which play a significant role in the cause of thermal pollution

1. Water as Cooling Agent in Power, Manufacturing and

Industrial plants

2. Soil Erosion:

3. Deforestation:

4. Urban runoff

5. Geological changes

1.6.4.2 Consequences of Thermal Pollution

The effects of thermal pollution on ecosystems are visualized as following ways

The warm water reduces the levels of DO in water causing suffocation for plants and animals. Warmer water allows rapid algae growth which in turn decreases DO levels. The constant flow of high temperature water induces toxins in water bodies. Aquatic kingdom may suffer from loss of appetite and biodiversity variations are accounted. Huge loss in aquatic population and their habitat with ecological imbalance are noticed.

1.6.4.3 Control of thermal pollution

- Heated water from the said sources may be controlled with cooling ponds which are designed for cooling by evaporation, convection, and radiation.
- Ciculating warmer water in cooling towers which transfer waste heat to the atmosphere through evaporation and heat transfer.
- Cogeneration process where waste heat is recycled for domestic or industrial heating purposes.

1.6.5 Radioactive Pollution

Radioactive fall-out from nuclear explosions and discharges from nuclear reactions, contains a number of radio-nuclides which emit radiations alpha beta and gamma particles which are highly harmful to mankind. They are unstable and do not persist for long time in the environment such as strontiumn-90 (half-life 28 years) and iodine-137. These radiation induces short-term and long-term hazards. The effect of all fall-outs carried away by are not only confined to explosion sites but also carried to other sites by wind, rain and snow.

1.6.5.1 Hazardous nature of nuclear radiations

Radioactive radiations are highly penetrating in nature with sufficient energy to damage living organisms thereby bringing disorder in

body. When living organisms are exposed to radioactive radiations the complex organic molecules present in the body get ionized and disrupts the normal functioning of the living organisms. Radiations damage the living organism by pathologically and genetically. Nuclear radiations may also reduce the effectiveness of enzymes. Moreover, there is a danger of certain elements to accumulate in certain specific organs of tissues.

Control measures:

(1) Proper steps should be taken to prevent the leakage of radioactive elements from nuclear reactors.

(2) The radioactive wastes should be stored till they decay completely

(3) Methods be adopted for the safe handling and disposal of radioactive materials.

Methods of disposal of radioactive wastes

Solid, liquid as well as gaseous radioactive wastes are produced different stages of nuclear fuel use. These must be disposed off in such a manner that they create no hazard to the human-beings and plants. The wastes can be disposed off in ground, air or ocean.

(1) Ground disposal is the cheapest and easy method, because soil absorbs radioactive materials easily. However, ground disposal is permitted only in area of low rain-fall and at points which are high above the general ground level in its vicinity. The radioactive waste containing calcium and strontium is first separated and then stored in separate tanks, which are buried in ground. They are kept in ground for 13 years and then, finally disposed off in the sea. Vacated coal-mines can also be used for waste disposal. The wastes are displosed off in the salt heaps provided in the mines, because salt is a powerful radioactive rays absorber

(2) Air: The disposal of radioactive gases into the air causes lot of trouble, because radioactive gases, particularly from iodine and strontium, are quite power full and absorbed by the plants, from there they enter into the human body, through the food. However, at present, amount of radioactive gases into air is much below the harmful level, but the problem may become of serious nature, when large number of reactors will come up in operation in near future. Generally, radioactive gases are stored in tanks, which are buried in the ground and finally disposed off in air, when sufficient low level of activity is attained.

NOTES

(3) Ocean is also employed for disposing off radioactive wastes. However, the activity level of radioactive waste should be below harmful level, before disposal otherwise activity of fish-life and sea-weed will be harmed. According to Dr. R.J. Hopkins, the solid wastes should be encased into concrete blocks, before dropping into sea.

1.7 Physiochemical and Biological Ivestigations of Water

The following are the water quality indices of water with reference to its physical, chemical and biological nature.

1.7.1 Physical Characteristics of Water

Physical characteristics of water temperature, colour, taste, odour and etc. are determined by senses of touch, sight, smell and taste. For example temperature by touch, colour, floating debris, turbidity and suspended solids by sight, and taste and odour by smell.

Solids

The total solids content of water is defined as the residue remaining after evaporation of the water and drying the residue to a constant weight at 103 °C to 105 °C. The organic fraction (or volatile solids content) is considered to be related to the loss of weight of the residue remaining after evaporation of the water and after ignition of the residue at a temperature of 500 °C. The volatile solids will oxidize at this temperature and will be driven off as gas. The inorganic (or fixed solids) remind as inert ash. Solids are classified as settleable solids, suspended solids and filterable solids. Settleable solids are the one that settle under the influence of gravity. Suspended solids and filterable solids are classified based on particle size and the retention of suspended solids on standard glass-fibre filters.

1.7.2 Chemical Characteristics of Water

The chemical characteristics of natural water are a reflection of the soils and rocks with which the water has been in contact. In addition, agricultural and urban runoff and municipal and industrial treated wastewater impact the water quality. Microbial and chemical transformations also affect the chemical characteristics of water

Major Cations

NOTES

Major cations found in natural water include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}). Calcium (Ca^{2+}), is the most prevalent cation in water which are estimated by flame photometric and EDTA methods

Major Anions

Major anions include chloride, sulfate, carbonate, bicarbonate, fluoride and nitrate. Bicarbonate (HCO_3^-) is the principal anion found in natural water. These ions are very important in the carbonate system, which provides a buffer capacity to natural water and is responsible in a great measure for the alkalinity of water. The concentration of the **chlorides** anions (Cl^-) determines the water quality. The **sulfates** anions (SO_4^{2-}) are frequently found in natural water as the result of the chemical dissolution, dissolve sulfur-content minerals and oxidize sulfates and sulfur:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2;$$

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4; \qquad (2.1)$$

$$2S + 3O_2 + 2\,H_2O = 2\,H_2SO_4.$$

Nitrate anions (NO_3) are found in natural water as the result of the bacteriological oxidation of nitrogenous materials in soil.

pH and Alkalinity

Alkalinity is defined as the capacity of natural water to neutralize acid added to it. Total alkalinity can be approximated by alkalinity as the following expression:

$$\text{Total alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (2.10)$$

Total alkalinity includes Hydroxide alkalinity [OH^-], Bicarbonate alkalinity [HCO_3^-] and Carbonate alkalinity [CO_3^{2-}]. If the pH and total alkalinity are measured, the concentration of the various components of alkalinity can be calculated using the values of α_1 and α_2 determined for the pH of the water. These values can be used to calculate the:

$$\text{Hydroxide alkalinity} = \frac{K_w}{[H^+]} \qquad (2.11)$$

NOTES

Bicarbonate alkalinity = $\alpha_1 C_t$

Carbonate alkalinity = 2 $\alpha_2 C_t$

where C_t is total carbonate and $C_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$.

Acidity

Acidity is the quantitative capacity of aqueous media to react with hydroxyl ions. Titration with a strong base (NaOH) to define end points (pH = 4 to 8). Acidity indicates the corrosiveness of acidic water on steel, concrete and other materials.

Inorganic Indicators of Water Quality

Some of the inorganic parameters include hardness, total dissolved solids, conductivity, and adsorption ratio.

Hardness

The ability of water to form lather with soap is defined as hardness. It represents total concentration of Ca^{2+} and Mg^{2+} ions. Other heavy metal ions may also contribute hardness. Hardness expressed as mg/L $CaCO_3$ is used to classify waters from soft to hard. Hardness is an indicator to industry of potential precipitation of calcium carbonates in cooling towers and boilers, interference with soaps and dyes in cleaning and textile industries and with emulsifiers in photographic development. Hard water is less corrosive than soft. Treatment usually left to consumer (domestic, industrial, etc) depending on needs.

Total Dissolved Solids

Total dissolved solids (TDS) is a measure of salt dissolved in a water sample after removal of suspended solids. TDS is residue remaining after evaporation of the water.

Organic Materials

Organic chemicals are made up of carbon (C), hydrogen (H), as well as nitrogen (N) and oxygen (O). Organic compounds also may contain sulfur (S), phosphorus (P), fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). Organic compounds in water also affect the water quality. Organic chemicals cause disagreeable tastes and odours in drinking water. Vinyl chloride, benzene and other organic contaminants are known carcinogenic agents, while chloroform is a cancer-suspect agent. For estimation of concentrations of organic materials, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand are determined

$$C_aH_bO_cN_dS_e + xO_2 \rightarrow aCO_2 + \tfrac{1}{2} bH_2O + dNO_3^- + eSO_4^- \qquad (2.13)$$

Biological Oxygen Demand

Biological oxygen demand (BOD), the most widely used parameter, is a measure of the amount of oxygen used by indigenous microbial population in water in response to the introduction of degradable organic material. This parameter depends on water characteristics: dilution, essential nutrients (N, P, K, Fe, etc), and bacteria seed. The 5-day BOD is most widely used. The BOD of natural water is related to the dissolved oxygen concentration, which is measured at zero time and after 5 days of incubation at 20 °C. The difference is the dissolved oxygen used by the microorganisms in the biochemical oxidation of organic matter. The BOD can be calculated as $BOD = D_0 - D_1$, in which the BOD_5 is in mg/L and D_0 and D_1 are the dissolved oxygen concentration in mg/L at time 0 and 5 days, respectively. Typical concentration of BOD for streams and rivers throughout the world are < 2 to 15 mg/ L and the observed range is < 2 to 65 mg/L.

Chemical Oxygen Demand

The chemical oxygen demand (COD) test of natural water yields the oxygen equivalent of the organic matter that can be oxidized by strong chemical oxidizing agent in an acidic medium. Potassium permanganate is the oxidizing chemical. Silver sulfate is added as a catalyst and to minimize the interference of chloride on the COD test. Mercuric sulfate is also added to inhibit interferences of metals on the oxidation of organic compounds. The reaction of the dichromate with organic matter is presented here in general way:

$$\text{Organic matter} + Cr_2O_7^{2-} + H^- \rightarrow 2Cr^{3+} + CO_2 + H_2O \qquad (2.14)$$

The COD observed in natural streams and rivers is < 2 mg/L to 100 mg/L.

Dissolved Oxygen

Typical dissolved oxygen concentrations observed in streams and rivers throughout the world are 3 to 8 mg/l. The observed range of dissolved oxygen concentrations is 0 mg/L to 19 mg/L. Dissolved oxygen is important in natural water because many microorganisms and fish require it in aquatic system. Dissolved oxygen also establishes an aerobic environment in which oxidized forms of many constituents in water are predominant. Under anoxic conditions in water, reduced forms of chemical species are formed and frequently lead to the release of undesirable odours until oxic conditions develop.

1.7.3 Biological Characteristics

NOTES

The principal groups of microorganisms in natural water include protists, plants and animals. The noticed micro organism in water are listed below

Kingdom	Representative members	Size, mm	Shape	Environmentally resistant stage
Animal	Crustaceans	--	--	--
	Worms	--	--	--
	Rotifers	--	--	--
Plants	Rooted aquatic plants	--	--	--
	Seed Plants	--	--	--
	Ferns	--	--	--
	Mosses	--	--	--
Protista	Protozoa	10^0-10^2	Variable	Cysts
	Algae	--	--	--
	Fungi (molds and yeasts)	10^0-10^2	Filamentous, coccoid	Spores
	Blue-green algae	10^0	Coccoid, filamentous	Cysts
	Bacteria	10^{-1}-10^1	Rod, coccoid, spiral comma	Spores, cystlike

Table 1.4 Simplified Classification of Microorganisms in Water

Plankton counting

A microscopic community of plants (phytoplankton) and animals (zooplankton), found usually free floating, swimming with little or no resistance to water currents. Phytoplankton (microscopic algae) usually occurs as unicellular, colonial or filamentous forms and is mostly photosynthetic and is grazed upon by the zooplankton and other organisms occurring in the same environment. Zooplankton principally comprise of microscopic protozoans, rotifers, cladocerans and copepods. The species assemblage of zooplankton also may be useful in assessing water quality. The structure of photosynthetic populations in the aquatic ecosystems is dynamic and constantly changing in species composition and biomass distribution.

Qualitative and quantitative evaluation of plankton

NOTES

Detailed analyses of phytoplanktonic populations are done by estimating the numbers in each species. The phytoplankton consisting of individual cells, filaments and colonies are counted as individual cells. When colonies of species are counted, the average number of cells per colony is counted, and in filamentous algae, the average length of the filament has to be determined. Preserved samples in bottles are mixed uniformly by gentle inversion and then exactly 1ml of the sample is pipetted out into the S-C cell for microscope analysis. The Sedgwick-Rafter cell is a devise used for plankton counting and is about 50mm long by 20mm wide and 1mm deep. The cell is covered by a relatively thick cover slip and is calibrated to contain exactly 1.0 ml.

1.7.4 Water Quality

Water quality is determined by physical, chemical and microbiological properties of water. The water quality characteristics throughout the world are characterized as per their own standards. The quality of natural water sources used for different purposes should be analyzed by proper routine procedures as water quality index and specification ranges are decided by various nation on their own accord. Our specification for drinking water standards are decided by Bureau of Indian Standards.

1.8 Check Your Progress Questions

1. Define hazardous materials and their characteristics?
2. What is meant by Ozone Hole?
3. Explain Radioactive Pollution and their control measures.
4. What is TDS?

1.9 Answers to Check Your Progress Questions

1. Hazardous material is a common term constituting hazardous, chemical, infectious and medical wastes which are potentially harmful to human health and environment. Hazardous materials will have the following characteristic

- Inflammable
- Corrosive
- Liberates toxic gas upon reaction
- Toxic
- Medical waste

2. Ozone (O_3) is an allotrope of oxygen is produced in the upper layer of atmosphere from oxygen gas by the absorption of ultraviolet light.

NOTES

$$3O_2(g) \xleftrightarrow[\text{light}]{\text{Ultraviolet}} 2O_3(g)$$

Oxygen light Ozone

3. Radioactive fall-out from nuclear explosions and discharges from nuclear reactions, contains a number of radio-nuclides which emit radiations alpha beta and gamma particles which are highly harmful to mankind. They are unstable and do not persist for long time in the environment such as strontiumn-90 (half-life 28 years) and iodine-137. These radiation induces short-term and long-term hazards.

Control measures:

(1) Proper steps should be taken to prevent the leakage of radioactive elements from nuclear reactors.

(2) The radioactive wastes should be stored till they decay completely

(3) Methods be adopted for the safe handling and disposal of radioactive materials.

4. Total dissolved solids (TDS) is a measure of salt dissolved in a water sample after removal of suspended solids. TDS is residue remaining after evaporation of the water.

1.10 Summary

- Hazardous material is a common term constituting hazardous, chemical, infectious and medical wastes which are potentially harmful to human health and environment. A hazardous material is a substance or mixture of substances having properties capable of producing adverse effects on the health and safety. Hazardous materials include solid waste, hazardous substances, hazardous waste, hazardous chemicals and medical waste.
- Industrial revolution and over exploitation of carbon mineral for power generation increases the volume of greenhouse gases emitted into the atmosphere. CO2 gas in the atmosphere perform major role of heating up of the atmosphere, due to trapping of infrared rays from the sun.
- Physical characteristics of water temperature, colour, taste, odour and etc. are determined by senses of touch, sight, smell and taste. For example temperature by touch, colour, floating debris, turbidity and suspended solids by sight, and taste and odour by smell.
- The chemical characteristics of natural water are a reflection of the soils and rocks with which the water has been in contact. In addition, agricultural and urban runoff and municipal and industrial treated wastewater impact the water quality. Microbial and chemical transformations also affect the chemical characteristics of water.

NOTES

1.11 Keywords

Alkalinity is defined as the capacity of natural water to neutralize acid added to it.

Soil pollution is the addition of unwanted chemical substances to the soil system thereby suppressing the soil fertility. Any substance capable of changing the productive capacity of the soil is termed soil pollutant.

Biological oxygen demand (BOD), the most widely used parameter, is a measure of the amount of oxygen used by indigenous microbial population in water in response to the introduction of degradable organic material.

The quality of natural water sources used for different purposes should be analyzed by proper routine procedures as water quality index and specification ranges are decided by various nation on their own accord. Our specification for drinking water standards are decided by **Bureau of Indian Standards.**

1.12 Self-assessment questions and exercises

1. What is meant by Acid Rain and how its formed?
2. Explain the effects of Ozone Layer Depletion?
3. Discuss in detail about Thermal Pollution.
4. Define Plankton counting?

1.13 Further readings

1. AK De - Environmental chemistry, Wiley Eastern Ltd., Madras (1994).
2. M. S. Sethi - Environmental chemistry, Shri Sai Printographers, New Delhi (1994).
3. Clair N. Sawyer, Perry L. Mc Carty and G. F. Parkin - Chemistry for Environmental Engineering, McGraw Hill Inc. New York (1994).
4. P.C. Jain and M.Jain - Engineering Chemistry, Dhanpat Rai Publishing Company, New Dehli (2018).
5. Asthana, DK and Meera Asthana - A Textbook of Environmental Studies. S. Chand Publication, New Delhi (2014).

Unit- II Waste Water Treatment Methods

Structure

2.0 Introduction

Waste water is the liquid waste, which includes human and house-hold waste waters, industrial wastes, ground wastes, street washings and storm waters. Waste water besides about 90 percent water, contains organic and inorganic matters in dissolved, suspension and colloidal states. Sewage or waste water is usually grey green to grey-yellow in colour but it darkens rapidly with time due to its decomposition. Constituents of sewage are domestic sewage from public and private buildings, industrial and trade-wastes from manufacturing processes such as tanneries, slaughter-houses, distilleries, textile mills, laundries, chemical plants, etc.; sub-soil or ground water entering through sewer and storm water, which is rain water from houses, roads, etc.

2.1 Objective

After going through this unit you are able to

- Acquire knowledge about the ill effects of waste water
- Understand the various waste water treatment method
- Gain knowledge about activated sludgeprocess and trickling filter process

NOTE

2.2 Aerobic and Anaerobic Oxidations of Waste Water

Waste water contains both aerobic and anaerobic bacteria, which can bring about oxidation of organic compounds present in it. In presence of a good amount of dissolved or free oxygen, organic compounds undergo a process of oxidation brought about by aerobic bacteria and the oxidation products are inoffensive smelling, non-putrefying nitrites, nitrates, sulphates, phosphates, etc. This kind of oxidation of sewage is called "aerobic oxidation". On the other hand, when the dissolved or free oxygen supply is below a certain value, the sewage is called stale and anaerobic bacteria bring about putrefaction, producing methane, hydrogen sulphide, ammonium sulphide and phosphine, which give offensive odour. This kind of oxidation of sewage, is called anaerobic oxidation. It may be pointed here that in an anaerobic oxidation, the bacteria extract combined oxygen, contained in organic matter, nitrates, nitrites and sulphates of sewage. When the anaerobic decomposition is continuing, the sewage is known as "septic sewage."

2.3 Treatment Methods

From the public health point of view, it is important that the sewage, before its ultimate disposal either on land or "dilution in water, should be given a treatment, during which its harmful compounds are transformed into harmless compounds. The main objectives of sewage treatment are: (i) to render sewage inoffensive so that it causes no odour or nuisance; (ii) to reduce or eliminate danger to the public health by possible contamination of water supplies (like rivers, canals, etc.) and bathing areas (e.g., bond, etc.); (ii) to prevent the destruction of fish and other aquatic life in rivers, canals, etc. into which sewage discharge is generally made.

2.4 Pretreatment

It is, generally, carried out using the artificial treatment method. The basic features of this method are to reduce the solid contents of the sewage.

2.5 Preliminary Process

It causes removal of large and coarse solids, inorganic matter, suspended or floating in the sewage. This involves in passing the sewage through bar screens to remove large suspended floating matter and mesh screens to remove coarse solids, gravels, silt, etc. Then the water is subjected to settling process. Settling process removes greater proportion of the suspended inorganic and organic solids from the liquid sewage. Chemical treatment is sometimes given to sewage, just prior to

sedimentation. This results in more rapid and complete removal of suspended matter is ensured. The chemicals employed are alum, ferrous sulphate, etc. These produce large gelatinous flocs, which entrap finely divided organic matter and settle rapidly.

$Al_2(SO_4)_3 + 6\ H_2O \rightarrow 2Al(OH)_3\downarrow + 3\ H_2SO_4$ (at pH $\geq$5)

The chief value of adding chemical coagulant is its ability to remove colloidal materials.

2.6 Secondary or Biological Treatment Process

It is essentially an aerobic chemical oxidation or aeration process. In this process, sewage water is filtered through specially designed sprinkling filters, so that aerobic conditions are maintained all the times. During this aerobic oxidation process, the carbon of the organic matter is converted into CO_2; the nitrogen into NH_3 and finally into nitrites and nitrates. The dissolved bases, present in the sewage water, then form salts such as ammonium nitrite, ammonium nitrate, calcium nitrate, etc. Thus:

$$\underset{\text{Urea}}{NH_2CONH_2} \xrightarrow[\text{aerobic}]{\text{Oxidation}} CO_2 + 2NH_3$$

$$NH_3 \xrightarrow{\text{Oxidation}} HNO_3, HNO_2\text{, etc.}$$

$$HNO_3, HNO_2 \xrightarrow{\text{+Bases}} NH_4NO_2, NH_4NO_3, Ca(NO_2)_2$$

$$Ca(NO_3)_2, KNO_2\text{, etc.}$$

Trickling filters are mostly employed for this purpose. These are either rectangular or circular in shape and about 2 m deep. They are filled with either coarse, crushed rock or large anthracite coal or blast furnace slag or broken bricks or graded clinkers. The under drain system is provided in the bottom of bed to collect affluent. Sewage is delivered to the filters by means of a rotating distributor. The sewage is allowed to trickle over the filtering medium by means of rotating arm distributor. As the trickled sewage starts percolating down-wards, through the filtering media, microorganism present in sewage grow on the surface of aggregates, using organic material of the sewage as food. Aerobic conditions always prevail and purified sewage is removed from the bottom. The normal trickling filters remove about 85% BOD.

NOTE

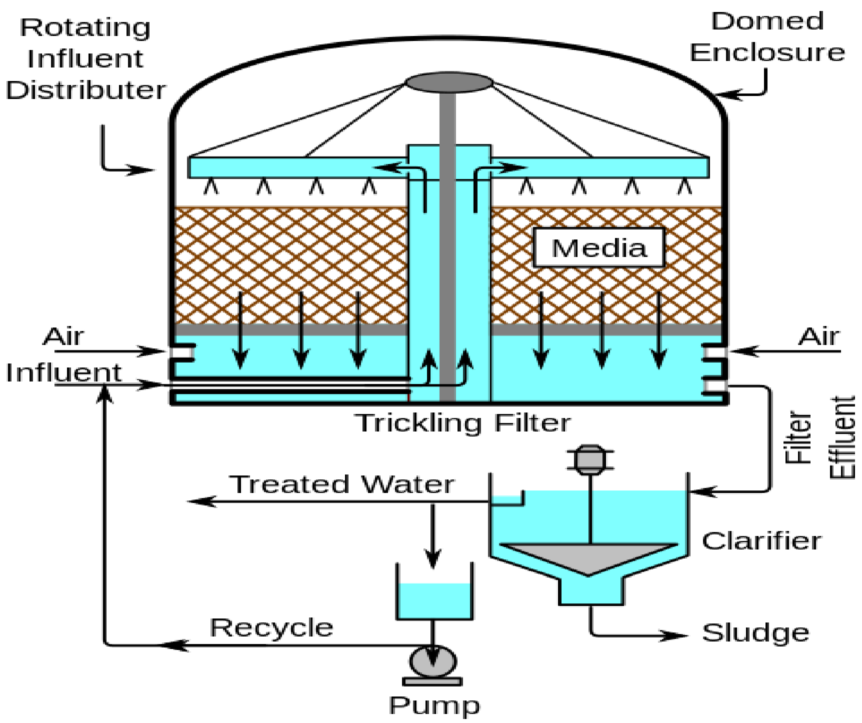


Figure 2.1 Trickling filter

Activated sludge process

Activated sludge process is based on the principle that adequate amount of oxygen or air is passed through sewage, containing aerobes. Complete aerobic oxidation occurs, though slowly. However, if this aeration is carried out in the presence of a part of sludge from the previous oxidation process, the oxidation process is much quickened. This so-added sludge from the previous process is known activated sludge.

The process consists in mixing the sedimented sewage with proper quantity of activated sludge and the mixture is then sent to the aeration tank, in which the mixed liquor is simultaneously aerated and agitated for 4 to 6 hours. During this aeration process, oxidation of the suspended organic matter takes place. First, oxidation of the carbon takes place, followed by that of nitrogen to nitrites and nitrates. After aeration, the affluent is sent to settling or sedimentation tank, where sludge is deposited and clean and non-putrefying liquid (practically free from bacterias, etc.) is drawn off. A part of the settled sludge is sent back for seeding fresh batch of sewage; while the remainder is disposed off by either : (i) sea-burial (i.e., dumping in se a), or (6) land spreading (i.e., spreading uniformly over soil, followed by ploughing in), or (c) digestion process. In (c), sludge is kept in a closed tank in the absence of air for a

prolonged period (about 30 days), when it suffers anaerobic decomposition, yielding gases like methane (about 60%), hydrogen sulphide, ammonium sulphide and phosphine. The gas can be used as fuel either for city supply or power generation. Between 400 to 600 litres of gas is produced from each kg of solid sludge.

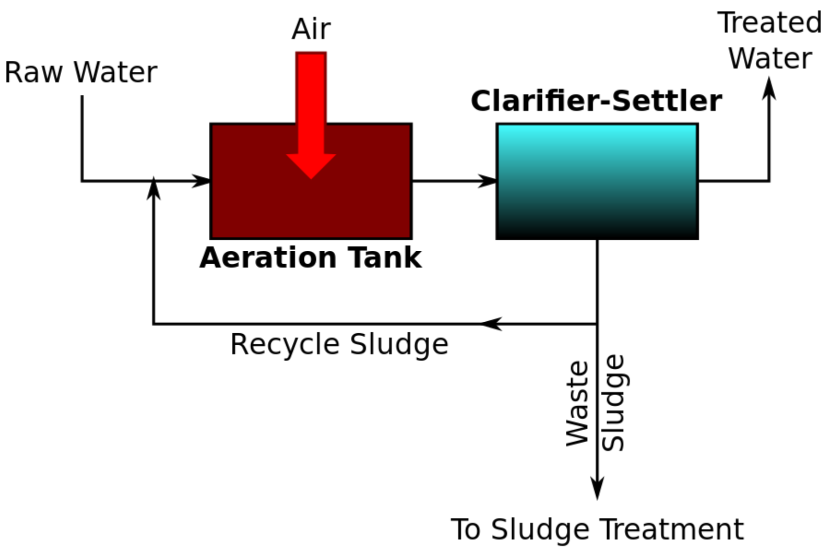


Figure 2.2 Activated sludge process

2.7 Tertiary/Advanced Methods of Waste Water Treatment

It is the most advanced phase of treatment and its objectives are to decrease the load of nitrogen and phosphorus compounds present in the effluents. It can be applied at any stage. It involves the following steps:

(i) Precipitation involves treatment of effluent from secondary treatment (or biological treatment) with calcium oxide (lime), which reacts with phosphorus compounds forming insoluble calcium phosphate, which settles down at the bottom of the tank, from where it is filtered off.

(i) Nitrogen stripping (to remove ammonia gas) is carried out (is directing the filtered water into a metal tower, containing a series of small baffle plates. Air is forced upwards through the trickling efficient, whereby ammonia gas is removed.

(ii) Chlorination involves treating the water from nitrogen stripping with chlorine so as to kill the disease-causing micro-organisms

NOTE

that might be present in sewage waste water. The so-treated water is then finally discharged into rivers/lakes, since it can be used after normal water treatment processes.

2.8 Check Your Progress Questions

1. Define the term pre treatment.
2. Write note on activated sludge process activated sludge.
3. Give an account on oxidation process.

2.9 Answers to Check Your Progress Questions

1. It is, generally, carried out using the artificial treatmentmethod. The basic features of this method are to reduce the solid contents of thesewage;

2. Activated sludge processis based on the principle that adequateamount of oxygen or air is passed through sewage, containing aerobes. Completeaerobic oxidation occurs, though slowly. However, if this aeration is carried out inthe presence of a part of sludge from the previous oxidation process, the oxidationprocess is much quickened. This so-added sludge from the previous process is known activated sludge.

3. During this aerobic oxidation process, the carbon of the organic matter is converted into CO_2; the nitrogen into NH_3 and finally into nitrites and nitrates.The dissolved bases, present in the sewage water, then form salts such as ammoniumnitrite, ammonium nitrate, calcium nitrate, etc. Thus:

$$\underset{\text{Urea}}{NH_2CONH_2} \xrightarrow[\text{aerobic}]{\text{Oxidation}} CO_2 + 2NH_3$$

$$NH_3 \xrightarrow{\text{Oxidation}} HNO_3, HNO_2, \text{etc.}$$

$$HNO_3, HNO_2 \xrightarrow{\text{+Bases}} NH_4NO_2, NH_4NO_3, Ca(NO_2)_2$$

$$Ca(NO_3)_2, KNO_2, \text{etc.}$$

2.10 Summary

- Waste water contains both aerobic and anaerobic bacteria, which can bring about oxidation of organic compounds present in it. In presence of a good amount of dissolved or free oxygen, organic compounds undergo a process of oxidation brought about by aerobic bacteria and the oxidation products are inoffensive smelling, non-putrefying nitrites, nitrates, sulphates, phosphates,

etc. This kind of oxidation of sewage is called "aerobic oxidation".

- The main objectives of sewage treatment are: (i) to render sewage inoffensive so that it causes no odour or nuisance; (ii) to reduce or eliminate danger to the public health by possible contamination of water supplies (like rivers, canals, etc.) and bathing areas (e.g., bond, etc.); (ii) to prevent the destruction of fish and other aquatic life in rivers, canals, etc. into which sewage discharge is generally made.
- Activated sludge process is based on the principle that adequate amount of oxygen or air is passed through sewage, containing aerobes. Complete aerobic oxidation occurs, though slowly. However, if this aeration is carried out in the presence of a part of sludge from the previous oxidation process, the oxidation process is much quickened. This so-added sludge from the previous process is known activated sludge.

2.11 Keywords

In presence ofa good amount of dissolved or free oxygen,organic compounds undergo a process of oxidation brought about byaerobic bacteria and the oxidation products are inoffensive smelling, non-putrefying nitrites, nitrates, sulphates, phosphates, etc. This kind of oxidation of sewageis called "**aerobic oxidation”**

The dissolved or free oxygen supply is below a certain value, the sewage is called stale and anaerobicbacteria bring about putrefaction, producing methane, hydrogen sulphide, ammoniumsulphide and phosphine, which give offensive odour. This kind of oxidation ofsewage, is called “**anaerobic oxidation”.**

When the anaerobic decomposition iscontinuing, the sewage is known as "**septic sewage.**"

2.12 Self-Assessment Questions and Exercises

1. What is preliminary process?
2. Explain about the secondary or biological treatment process.
3. Discuss about the purpose of Trickling filters.
4. Explain the tertiary or advanced methods of wastewater treatment.

NOTE

2.13 Further Readings

1. AK De - Environmental chemistry, Wiley Eastern Ltd., Madras (1994).
2. P.C. Jain and M.Jain - Engineering Chemistry, Dhanpat Rai Publishing Company, New Dehli (2018).
3. Subramanian V, (2002). A Text Book on Environmental Science. Narosa Publishing House. New Delhi.
4. Abbasi SA, (1998). Environmental pollution and its control, Cogent international, Pondicherry Suresh K.
5. Best GA, (1999). Environmental Pollution Studies. Liverpool University Press.

Unit- III Electrochemical Power Sources Structure

Structure

3.0 Introduction

Rapid utilization of various resources such as coal, oil and petroleum etc.,and alarming environmental safety causes continuous threat to find an energy alternative. These efforts results in prospect of electrochemical power sources. The widespread application of such electrochemical driven power sources provides a cleaner environment with reduction in the rate of accumulation of greenhouse gases. The success of this technology is the use of electrochemical power sources such as batteries, fuel cells and super capacitors which can convert chemical energy to electrical energy more efficiently and quietly than internal combustion engines.

3.1 Objectives

After going through this you are able to

- appreciate the application of electrochemistry
- distinguish different types of electrochemical power sources
- comprehend the concept of super capacitor

NOTE

3.2 Principle of Energy Conversion

The transformation of energy from one form to the other is always governed by the laws of thermodynamics. All energy transformation involves the utility of four laws of thermodynamics. The energy conversion is facilitated by the decrease of change in free energy accompanied with changes in enthalpy and entropy. Basically the first law of thermodynamics directly illustrates clearly about the energy transformation process. Thus the various available energies such as wind energy, light energy, sound energy, tidal energy, geothermal energy, electrical energy, chemical energy, mechanical energies are inter convertible according to the loss of thermodynamics

3.3 Electrochemical Energy Conversion

The conversion electrical energy to chemical energy and vice versa is always possible under the light of thermodynamics. The conversion involves decrease in free energy value as connected to the potential of the constructed cell as follows

$\Delta G = -n\ f\ E$

Where ΔG – free energy change

n- number of electrons involved in the redox process

f- faraday; 96,495 columbs

E – potential developed by the cell in Volts

3.4 Classification of Batteries

A device which stores and converts chemical energy into electrical energy is called as battery. Batteries are classified as

(i) Primary batteries in which the cell reaction is not reversible.

(ii) Secondary battery in which the cell reaction are reversed

(iii) Flow battery and fuel cell is an electrochemical cell that converts chemical to electrical energy.

3.4.1 Primary and Secondary Systems

A few kinds of primary and secondary systems are discussed here.

Dry (or Laclanche) cell

It is a cell without fluid component and example for primary batteries. The anode of the cell is zinc) containing an electrolyte consisting of NH_4Cl, $ZnCl_2$, and MnO_2, to which starch is added to make it thick paste-like so that it is less likely to leak. A carbon (graphite) rod serves as the cathode; which is immersed in the electrolyte in the centre of the cell. The anode (oxidation) half-reaction is:

NOTES

Oxidation: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$
(At anode)

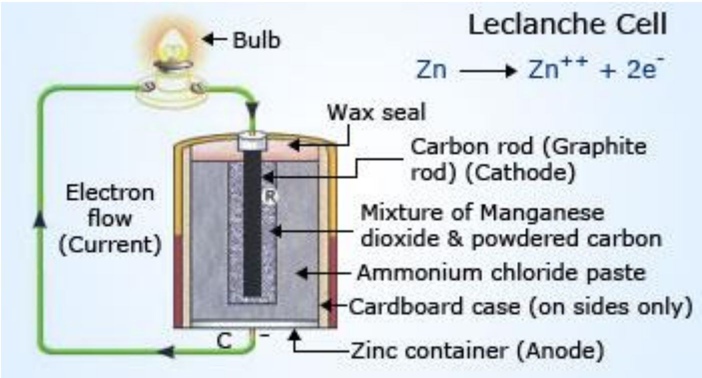


Figure 3.1 Leclanche Cell

The cathode reaction involves the reduction of MnO_2, to a series of compounds having Mn in +3 oxidation state.

Reduction: $2\ MnO_2\ (s) + H_2O + 2e^- \rightarrow Mn_2O_3\ (s) + 2OH^-$ (aq)

The dry cell is a primary cell, since various reactions involved cannot be reversed by passing electricity back through the cell. Dry cell is cheap to make, and gives a voltage of about 1.5V. But it has two significant disadvantages: (i) When current is drawn rapidly from it, products build up on the electrodes thereby causing drop in voltage ; (ii) Since the electrolytic medium is acidic, so zinc metal dissolves slowly, thereby the cell run down slowly, even if it is not in use. Dry cell finds applications in flash-lights, transistor radios, calculators, etc.

Alkaline battery is an improved form of the dry cell which of primary nature and employs KOH as its electrolyte. In this battery, zinc taken as powdered form is mixed with KOH to get a gel. Graphite rod is surrounded by a paste containing MnO_2. The outside body is made of zinc. The cell reactions are :

Anode : $Zn\ (s) + 2OH^-\ (aq) \rightarrow Zn(OH)_2\ (s) + 2e^-$

Cathode: $2\ MnO_2\ (s) + H_2O\ (l) + 2e^- \rightarrow Mn_2O_3\ (s) + 2\ OH^-\ (aq)$

Net reaction: $Zn\ (s) + 2\ MnO_2\ (s) + H_2O\ (l) \rightarrow Zn(OH)_2\ (s) + Mn_2O_3\ (s)$

The main advantages of alkaline battery over dry battery are : (i) zinc does not dissolve as readily in a basic medium, (ii) the alkaline battery maintains better its voltage as the current is drawn from it, (iii) the life of alkaline battery is longer than dry cell, since there is no

NOTE

corrosion of Zn. Alkaline batteries find used in camera exposure controls, calculators, watches, etc.

Nickel-cadmium (nicad) battery consists of a cadmium anode and a cathode composed of a paste of NiO(OH) (s). The cell reaction are :

Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Net reaction: $2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

The reaction can be readily reversed, because the reaction products, $Ni(OH)_2$ (s) and $Cd(OH)_2$ (s), adhere to the electrode surfaces. It is used in electronic calculators, electronic flash units, cordless electronic shavers, transistors and other battery powered small tools.

LEAD-ACID STORAGE CELL

A storage cell is one that can operate both as a voltaic cell and as an electrical cell. When operating as a voltaic cell, it supplies electrical energy. The common example of a storage cell is the lead-acid storage cell. One of its electrodes is made of lead. The other electrode is made of lead dioxide (PbO_2) or rather a paste of PbO_2, is pressed into a grid, made of lead. A number of lead plates (-ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel. The lead plates fits in-between the lead dioxide plates. Various plates are separated from the adjacent ones by insulators like strips of wood or rubber or glass fibre. The entire combination is then immersed in dil.H_2SO_4, corresponding to a density of 1.2 to 1.3.

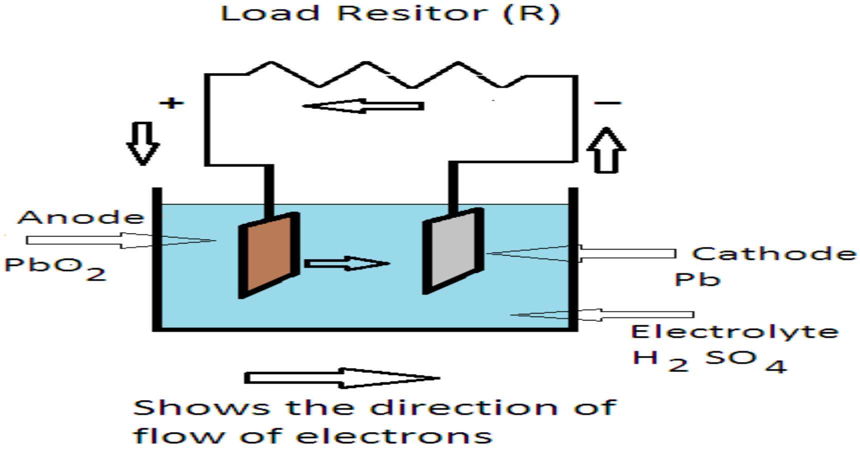


Figure 3.2 Lead - Acid Storage Cell

NOTES

Discharging: When the storage cell is operating as a voltaic cell (i.e., for supplying electrical energy), it is said to be discharging. The lead electrode loses electrons, which flow through the wire.

In this reaction, oxidation of lead takes place at the anode.

$$Pb \rightarrow Pb^{2+} + 2e^- \qquad \text{(At lead anode)}$$

The Pb^{2+} ions then combine with sulphate (SO_4^{2-}) ions.

$$Pb^{2+} + SO_4^{2+} \rightarrow PbSO_4 \downarrow$$

The electrons released from the anode (lead plate) flows to the dioxide electrode. Here PbO_2 gains electrons to form Pb^{2+} ions. In other words, lead undergoes reduction at the cathode from oxidation state +4 to +2. The Pb^{2+} ions then combine with SO_4^{2-} ions.

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2\,H_2O \qquad \text{(At } PbO_2 \text{ cathode)}$$

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow$$

So, the net reaction during use (or discharging) is:

$$Pb + PbO_2 + 4H^+ + 2\,SO_4^{2-} \rightarrow 2\,PbSO_4 \downarrow + 2H_2O + Energy$$

It may be noted that lead sulphate is precipitated at both the electrodes. The voltage of each cell is about 2.0 volts at a concentration of 21.4% H_2SO_4 at 25°C. Lead cell, commonly used in automobiles, is a combination of six such cells in series to form a battery with an e.m.f. of 12 volts. During charging the above said reactions are reversed.

3.5 Basic Electrochemical Reaction and Performance Primary and Secondary Systems

In any electrochemical system energy is harvested due to redox reaction. The anode undergoes oxidation with liberation of electrons. These electron flow in a closed loop and reaches the cathode and reduces the cathodic ions. The current flows in opposite direction of electron flow and completes the circuit. The primary source serves as instant power producer and exhibit good performance during discharge. However the amount of potential developed during discharge is limited and needs much attention. However the secondary system delivers better results and much provides sounding performance. It can act as both electrolytic cell during recharging and electrochemical cell during discharging.

NOTE

3.5.1 Fuel Cells

3.5.1.1 Introduction

In a fuel cell, electric energy is obtained without combustion of oxygen A fuel cell converts the chemical energy of the fuels directly into electricity. The essential process in a fuel cell is:

Fuel + Oxygen → Products + Electricity

One of the simplest and most successful fuels is hydrogen-oxygen fuel cell. It consists essentially (see Fig. 22) of an electrolytic solution such as 25% KOH solution, and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment respectively, where the following reactions take place:

Anode: $2H_2\,(g) + 4\,OH^-\,(aq) \rightarrow 4\,H_2O\,(l) + 4\,e^-$

Cathode: $O_2\,(g) + 2H_2O + 4e^- \rightarrow 4\,OH^-\,(aq)$

Net : $2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$

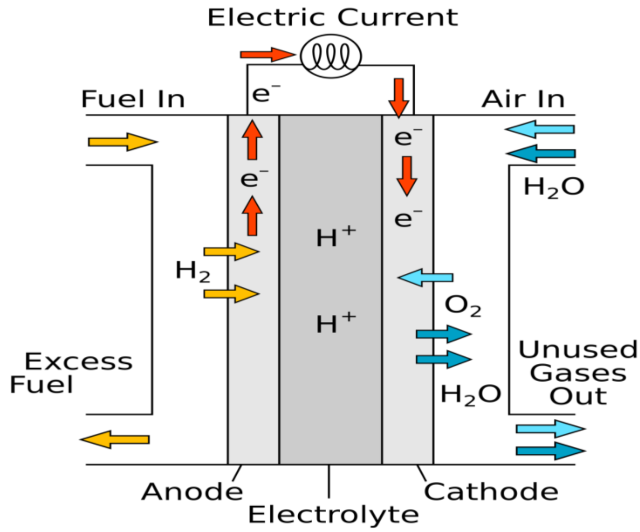


Figure 3.3 Hydrogen-oxygen fuel cell

The standard emf of the cell,

$$E^o = E^o_{ox} + E^o_{red} = 0.83\text{ V} + 0.40\text{ V} = 1.23\text{ V}.$$

In actual practice, the emf of cell is 0.8 to 1.0 V. It may be noted that the only product discharged by the cell is water. Usually, a large number of these cells are stacked together in series to make a battery, called fuel cell battery or fuel battery. Electrolytes used for most often are aqueous KOH or H_2SO_4 or ion-exchange resin saturated with water.

For low-temperature operating fuel battery (-54°C to 72°C), potassium thiocyanate dissolved in liquid ammonia is employed.

Application : Hydrogen-oxygen fuel cell are used as auxiliary energy source in space vehicles (eg., Apollo spacecraft), submarines or other military-vehicles. The weight of the fuel battery sufficient for 15 days is space is approximately 250 kg. This may be compared to the several tonnes that would have been required for an engine-generator set. In case of H_2 /O_2 fuel cells, the product water proved to be a valuable source of fresh water by the astronauts.

3.5.1.2 Types of fuel cells:

In addition to the H_2/O_2 system, a number of other fuel cells have developed. Among these are :

(i) Propane-oxygen fuel cell:

The half-reactions are:

Anode: $C_3H_8\ (g) + 6\ H_2O\ (l) \rightarrow 3\ CO_2\ (g) + 20\ H^+ + 20\ e^-$

Cathode: $5\ O_2\ (g) + 20\ H^+\ (aq) + 20\ e^- \rightarrow 10\ H_2O\ (l)$

Net reaction: $C_3H_8\ (g) + 5\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 4\ H_2O\ (l)$

(ii) Methyl alcohol-oxygen fuel cell:

The half-reactions are:

Anode: $CH_3OH\ (l) + H_2O\ (l) \rightarrow CO_2\ (g) + 6H^+\ (aq) + 6\ e^-$

Cathode: $3/2\ O_2\ (g) + 6\ H^+\ (aq) + 6e^- \rightarrow 3H_2O\ (l)$

Net reaction: $CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$

Other potential uses include the conversion of coal and petroleum into CO plus H_2 mixture, followed by oxidizing it in a fuel cell. However, commercial exploitation of such fuel cells is finding obstructions of developing proper electrodes for carrying out the energy conversion efficiently.

(iii) **Phosphoric acid fuel cells** s use liquid phosphoric acid as the electrolyte. The electrodes are made of carbon paper coated with a finely-dispersed platinum catalyst. The catalyst strips electrons off the hydrogen-rich fuel at the anode. Positively charged hydrogen ions then migrate through the electrolyte from the anode to the cathode. Electrons generated at the anode travel through an external circuit, providing direct current electric power, and return to the cathode. There the electrons, hydrogen ions and oxygen form water, which is discharged from the

NOTE

cell.Phosphoric acid fuel cells operate at around 150 to 200°C above the boiling point of water. Phosphoric acid fuel cells have been installed and shown to be reliable suppliers of premium power.

(iv) **Molten carbonate fuel cells** are a class of second generation fuel cells designed to operate at higher temperatures than phosphoric acid or proton exchange membrane fuel cells. Molten carbonate technology can achieve higher fuel-to-electricity and overall energy use efficiencies than lower temperature cells. In a molten carbonate fuel cell, the electrolyte is made up of lithium-potassium carbonate salts heated to about 650°C. At these temperatures, the salts melt into a molten state that can conduct charged particles, called ions, between two porous electrodes. At the anode, hydrogen reacts with the carbonate ions (CO_3^{2-}) to produce water, carbon dioxide, and electrons. The electrons travel through an external circuit - creating electricity - and return to the cathode. There, oxygen from the air and carbon dioxide recycled from the anode react with the electrons to form CO_3^{2-} ions that replenish the electrolyte and transfer current through the fuel cell, completing the circuit.

Anode reaction: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

(v) **Solid polymer electrolyte fuel cell** or proton exchange membrane fuel cell (PEFC) offers an order of magnitude higher power density than any other fuel cell system. The PEFC can operate on reformed hydrocarbon fuels, with pretreatment, and on air. The use of a solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Its low operating temperature provides instant start-up and requires no thermal shielding to protect personnel. The PEFC uses as its electrolyte a polymer membrane, which is an electronic insulator, but an excellent conductor of hydrogen ions. The materials used consist of a fluorocarbon polymer backbone, similar to Teflon, to which are attached sulfonic acid groups. The acid molecules are fixed to the polymer and cannot "leak" out, but the protons on these acid groups are free to migrate through the membrane. With the solid polymer electrolyte, electrolyte loss is not an issue with regard to stack life.

The anode and cathode are contacted on the back side by flow field plates made of graphite in which channels have been formed. Hydrogen from the fuel gas stream is consumed at the anode, yielding electrons to the anode and producing hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons (from the

cathode) and hydrogen ions (from the electrolyte) to produce water. The water does not dissolve in the electrolyte and is, instead, rejected from the back of the cathode into the oxidant gas stream. As the PEFC operates at about 80° C, the water is produced as liquid water and is carried out of the fuel cell by excess oxidant flow.

(vi) Solid oxide fuel cells (SOFC) differ in many respects from other fuel cell technologies. First, they are composed of all-solid-state materials - the anode, cathode and electrolyte are all made from ceramic substances. Second, because of the all-ceramic make-up, the cells can operate at temperatures as high as 1,000^oC significantly hotter than any other major category of fuel cell. At the high operating temperatures, oxygen ions are formed at the "air electrode" (the cathode). When a fuel gas containing hydrogen is passed over the "fuel electrode" (the anode), the oxygen ions migrate through the crystal lattice to oxidize the fuel. Electrons generated at the anode move out through an external circuit, creating electricity. Reforming natural gas or water gas (H_2 + CO or other hydrocarbon fuels to extract the necessary hydrogen can be accomplished within the fuel cell, eliminating the need for an external reformer.

In such a fuel, reformate gas (H_2 + CO) is used as a fuel and oxygen as the oxidant.

Anode reaction: $xH_2 (g) + yCO (g) + (x+ y)O^{2-} \rightarrow xH_2O + y CO_2 (g) + 2(x + y) e^-$

Cathode reaction: $\frac{1}{2}(x+ y) O_2 (g) + 2(x+y)e^- \rightarrow (x+ y)O^{2-}$

The reaction rate at the operating temperature (about 1,000° C) is quite high, so no noble metal catalyst is needed. Moreover, carbon monoxide does not poison the electrodes.

(vii) **Biochemical fuel cell consists** of organic substrate (e.g., glucose, urea), which acts a fuel (at cathode), which is oxidized by living organisms (e.g., bacteria or enzymes derived from bacteria). These living organisms thus act as bio-anodes. Direct reduction of oxygen (or some other oxidant) at the bio cathode is also possible. Moreover, the biological system can be employed to generate reactant which is being consumed at the cathode, e.g., pseudomonas mathranics bacteria are capable of utilizing the carbon from methanol (or methane), there by liberating hydrogen, which in-turn can be utilized as a fuel. Biochemical fuel cells thus produce electricity and at the same time, control pollution, due to organic wastes.

Advantages of fuel cells :

NOTE

They do not store chemical energy resembles an engine more than does a battery. The fuel cell does not operate like an engine and not subject to thermodynamic limitations in energy conversion. The efficiency of a fuel cell is about twice that of a conventional power plant for generating electricity. In addition, fuel cell generators are free of the noise, vibration, heat transfer, thermal pollution, and other problems normally associated with conventional power plants.

3.6 Supercapacitors

Super capacitors or ultra-capacitors are unique devices exhibiting 200 times larger capacitance than a conventional capacitor which consists of two plates separated by a gas or vacuum as the dielectric. When a metal (or an electronic conductor) is brought in contact with a solid or liquid ionic conductor, a charge accumulation is achieved electrostatically on either side of the interface leading to the development of an electrical double-layer, which is essentially a molecular dielectric. Two types of super capacitors have been developed and tested. One operates, by charging and discharging of the interfacial electrical-double-layer. In the second type, often called as pseudo capacitors or redox capacitors, the charge discharge mechanism involves the transfer of electric charge between the phases but without any bulk-phase transformation. The electrons involved in the non-faradaic electrical-double layer charging are the itinerant conduction-band electrons of the metal or carbon electrode while the electrons involved in the faradaic processes are transferred to or from valence-electron states (orbitals) of the redox cathode or anode reagent.

3.7 Check Your Progress Questions

1. What is electrochemical energy conversion.
2. What are batteries?
3. Give the classification of batteries.
4. Write a note on H_2/O_2 fuel cell.
5. Define the super capacitor.

3.8 Answers to Check Your Progress Questions

1. The conversion electrical energy to chemical energy and vice versa is always possible under the light of thermodynamics. The conversion involves decrease in free energy value as connected to the potential of the constructed cell as follows

$\Delta G = -n f E$

2. A device which stores and converts chemical energy into electrical energy is called as battery.

3. Batteries are classified as given below:

(i) **Primary batteries** in which the cell reaction is not reversible.

(ii) **Secondary battery** in which the cell reaction are reversed
(iii)**Flow battery** and fuel cell is an electrochemical cell that converts chemical to electrical energy.
4.Hydrogen-oxygen fuel cell are used as auxiliary energy source in space vehicles (eg., Apollo spacecraft), Submarines, or other military-vehicles.
5. Super capacitors or ultra-capacitors are unique devices exhibiting 200 times larger capacitance than a conventional capacitor which consists of two plates separated by a gas or vacuum as the dielectric.

3.9 Summary

- When the storage cell is operating as a voltaic cell (i.e., for supplying electrical energy), it is said to be discharging.
- The dry cell is a primary cell, since various reactions involved cannot be reversed by passing electricity back through the cell. Dry cell is cheap to make, and gives a voltage of about 1.5V.
- Hydrogen-oxygen fuel cell are used as auxiliary energy source in space vehicles (eg., Apollo spacecraft), submarines or other military-vehicles. The weight of the fuel battery sufficient for 15 days is space is approximately 250 kg.
- Solid oxide fuel cells (SOFC) differ in many respects from other fuel cell technologies. First, they are composed of all-solid-state materials - the anode, cathode and electrolyte are all made from ceramic substances.
- Super capacitors or ultra-capacitors are unique devices exhibiting 200 times larger capacitance than a conventional capacitor which consists of two plates separated by a gas or vacuum as the dielectric.

3.10 Keywords

- The **energy conversion** is facilitated by the decrease of change in free energy accompanied with changes in enthalpy and entropy.
- **Battery:** A device which stores and converts chemical energy into electrical energy
- **Alkaline battery** is an improved form of the dry cell which of primary nature and employs KOH as its electrolyte.
- **A storage cell** is one that can operate both as a voltaic cell and as an electrical cell.

3.11 Self-Assessment Questions and Exercises

1. Explain about Dry (or Laclanche) cell.
2. Write about the charge-discharge reaction of lead-acid storage cell
3. Discuss about the basic electrochemical reaction primary and secondary systems
4. Give a brief review about fuel cells and its types.

NOTE

5. Which states are involve in the Super capacitor?

3.12 Further Readings

1. D.R. Crow, Principles and application of electrochemistry, Chapman and Hall (1988).
2. P.C. Jain and M.Jain - Engineering Chemistry, Dhanpat Rai Publishing Company, New Dehli (2018).
3. D.P.letcher and F.C. Walsh - Industrial Electrochemistry, Vol. II, Blakrid Academic Professional, London, (1993).
4. Modern Electrochemistry 1. Volume 1 and 2, by J. O'M. Bockris and A. K. N. Reddy, Kluwer Academic, (2000).

NOTES

Block -2: ElectroChemistry - I

Unit -4: Corrosion

Structure

4.0 Introduction

Many metals exist in nature in combined forms such as oxides, carbonates, hydroxy carbonates, sulphides, sulphates, chlorides and silicates. During the extraction processes, the metallic ores are reduced to their metallic states. During extraction of metals, considerable amounts of energy are employed to isolated pure metals present in the excited state from their corresponding ores in lower energy state. Thus the isolated metals have a natural tendency to get back to original combined state. When metals are applied for usage in various forms, they are exposed to harsh environments (such as dry gases, moisture, liquids, etc), the exposed metal surfaces begin to deteriorate into more stable metal compounds. The kinetics is more rapidly when they come in contact with gaseous and/or liquid environment (or surroundings). In other words, destruction or deterioration of the metal starts at the surface. This type of

NOTE

metallic destruction may be due to direct chemical attack or electrochemical attack.

4.1 Objectives

After going through this unit, you are able to

- understand phenomenon of corrosion process
- appreciate the mechanism of corrosion process
- recognize the various forms of corrosion

4.2 Basics Aspects of Corrosion

It is process of deterioration or destruction metallic surface with consequent loss of a solid metallic material, through a chemical or electrochemical attack by its environment is called as corrosion. Corrosion is a "**reverse process of extractive metallurgy**”. The most familiar example of corrosion is rusting of iron, when exposed to the atmospheric conditions. During this process, a layer of reddish scale and powder of oxide Fe_3O_4 is formed and the iron becomes weak. Another common example is formation of green film of basic carbonate $CuCO_3$ and $Cu(OH)_2$ on the surface of copper, when exposed to moist-air containing carbon dioxide.

4.3 Importance of Corrosion Studies

The process of corrosion is slow and occurs only at surfaces of metals. But the losses resulted due to corrosion processes are enormous which are visualized as destruction of machines, equipment and different types of structural damages. Losses occurring due to corrosion are measured as both in terms of the cost of metals and cost of fabricating equipment’s, machine tools and structures. Corrosion causes wastage of energy, money and human resources. Corrosion produces a regular impact on the gross national product (GNP) of every nation. In 1971, Hoar reported to UK government that a good fraction of corrosion failures were avoidable and improved literacy on corrosion education was a good way of tackling the problem. As per 1995 survey, corrosion of metals resulted in a loss of 300 billion dollars per year in U.S.A. alone. Cost attributed to the corrosion damages has been estimated to be of the order of 3 to 5 percent of gross national product of industrialized countries out of which 1 to 2 percent can be reduced using proper technology of corrosion control. According to Indian chapter of National Association of Corrosion Engineers International, India is footing an annual bill close to Rs 2.5 lakh crores on account of losses due to corrosion. The cost works out to be much higher than any of the calamities the nation has faced over the years.

Direct losses and indirect losses are the two ways by which corrosion damages can be quantified. The direct losses are the cost of substituting corroded structures and machineries or their components, such as condenser tubes, mufflers, pipelines and metal roofings including necessary labour. Direct losses include the extra cost of using corrosion resistant metals and alloys instead of carbon steel which has adequate mechanical properties but not sufficient corrosion resistance. There are also the costs of galvanizing or nickel plating of steel, of adding corrosion inhibitors, or of dehumidifying storage rooms for metallic equipments. Indirect losses are more difficult to assess which may be either economical or social in origin. These may include, contamination of the product, loss of valuable product from a container that has corroded through, damage of equipment adjacent to that in which corrosion failure occurs, loss of production, safety (eg: sudden failure of equipment may cause fire, explosion or release of toxic products) and appearance.

Many serious accidents and explosions were initiated by corrosion of critical components causing environmental pollution, personal injury and death. Some of the noteworthy havocs caused due to corrosion were Sewer explosion, loss of USAF F16 fighter aircraft, the Aloha aircraft incident, MV KIRKI tragedy. The above narration is a pointer to the need for creating public awareness about corrosion and its losses, so that at least half of the losses could be prevented by suitable intervention. The cost of the corrosion problem may be made clear by the approximate estimate of loss of metal due to corrosion, as 7 to 8.5 billion dollars per annum all-over the world. Hence there is great upsurge for understanding the mechanism of corrosion to control its ill effects. Moreover, it is better to avoid harsh corrosion conditions and provide simultaneously protection against corrosion.

4.4 Emf and Galvanic Series

4.4.1 Electrochemical Series

The arrangement of standard reduction electrode potential of elements in the increasing order is called as electrochemical series. In the electrochemical series a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example, lithium present in the top of the series corrodes faster than magnesium available later in the series. Similarly copper corrodes faster than silver. Thus by using the data present in the series prediction of corrosion process of various elements is possible. Moreover, ease of redox nature, relative displacement tendency, spontaneity of chemical reaction and determination of equilibrium constants are also determined using the series.

4.4.2 Galvanic Series

The series was developed by studying corrosion of metals and alloys in unpolluted sea-water without their oxide films. Exceptions in electrochemical series are accounted in galvanic series. For example, Ti above Ag in the electrochemical series is less reactive than Ag and in Zn-Al couple, Al acts as cathode and is protected. These observations are explained in the view of galvanic series.

Electrochemical series	Galvanic series
Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration.	The series was developed by studying corrosion of metals and alloys in unpolluted sea-water without their oxide films
The position of given element is fixed	The position of a given metal may shift
It does not give any information regarding positions of alloys.	Alloys are included in galvanic series
The series comprises of metals and non-metals.	The series comprises of metals and alloys.
It predicts the relative displacement tendencies.	It predicts the relative corrosion tendencies.

Table 4.1 Difference between Electrochemical and Galvanic Series

From the above table, it is clear that electrochemical series does not account for the corrosion of all metals and alloys. Consequently, a more practical series, called galvanic series have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water. Thus, galvanic series give real and useful information's for studying the corrosion of metals and alloys.

Active (or anodic) ↑	1. Mg 2. Mg alloys 3. Zn 4. Al 5. Cd 6. Al alloys 7. Mild steel

NOTES

	8. Cast iron
	9. High Ni cast iron
	10. Pb-Sn solder
	11. Pb
	12. Sn
	13. lconel
	14. Ni- Mo- Fe alloys
	15. Brasses
	16. Monel
	(7 = Ni, 30 = Cu, rest = Fe)
	17. Silver solder
	18. Cu
	19. Ni
	20. Cr stainless steel
	21. 18 - 8 stainless steel
	22. 18 - 8 Mo stainless steel
	23. Ag
	24. Ti
	25. Graphite
	26. Au
	27. Pt
Noble (or cathodic)	

Table 4.2 Galvanic series.

4.5 Classification of Corrosion

The corrosion processes are classified as chemical and electrochemical type.

NOTE

4.5.1 Chemical or Dry Corrosion

The direct chemical action of environmental gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid on immediate proximity metal surfaces is termed as chemical corrosion. Chemical corrosion are further classified as

- Oxidation corrosion
- Corrosion by other gases
- Liquid metal corrosion

4.5.1.1 Oxidation corrosion

The direct action of oxygen on metal surface in the absence of moisture at low or high temperatures causes oxidation corrosion. Alkali metals viz., Li, Na, K. Rb, and alkaline-earths viz., Be, Ca, Sr, are rapidly oxidized at normal temperatures. All metals except coinage metals are oxidised at higher temperatures.

The reactions in the oxidation corrosion are:

$$2\,M \rightarrow \underset{\text{Metal ions}}{2\,M^{n+}} + 2\,n\,e^- \quad \text{(Loss of electrons)}$$

$$\frac{n}{2} O_2 + 2ne^- \rightarrow \underset{\text{Oxide ions}}{n\,O^{2-}} \quad \text{(Gain of electrons)}$$

Finally,

$$2M + \frac{n}{2} O_2 \rightarrow \underbrace{\underset{\text{Metal ions}}{2\,M^{n+}} + \underset{\text{Oxide ions}}{n\,O^{2-}}}_{\text{Metal Oxide}}$$

Nature of the oxide formed plays an important part in oxidation corrosion process. Oxidation occurs initially at the surface of the metal and the resulting metal oxide scale forms a surface film. Further, the oxidation will take place by diffusion of either the metal or the oxygen through the scale facilitating corrosion. The diffusion of ions through the oxide barrier is decided by nature of surface film.

Metal + Oxygen → Metal oxide (corrosion product)

(i) **Stable film:** A stable film gets adhered tightly to the parent metal surface and the formed layer is of impermeable nature thereby shielding the metal surface .The oxide films of metals such as Al, Cu, Sn, Pb and Pt are stable, tightly-adhering and impervious in nature.

(ii) **Unstable film:** Oxide layer formed gets decomposed back into the metal and oxygen and oxidation corrosion is not further possible. Metals viz.,Ag, Au, and Pt forms these type of layers.

Metal oxide ↔ Metal + Oxygen

(iii) **Volatile film:** The oxide layer volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. E.g., Molybdenum (MoO_3) is a volatile layer.

(iv) **Porous film:** This type of oxide layer have pores and cracks favoring oxygen access to the underlying surface of metal leaving corrosion unbarred and the said process continues till the entire metal is completely converted into its oxide.

4.5.1.2 Corrosion by other gases

Gases likely SO_2, CO_2, Cl_2, H_2S, F_2, etc. will have corrosive effect on metals based on latter's chemical affinity. The degree of attack depends on the formation of protective or non-protective films on the metal surface. If the film formed is protective or non-porous the extent of attack decreases and controls corrosion. E.g., AgCl film, resulting from the attack of Cl_2 on Ag. If the formed film is non-protective or porous then the whole metal gets destroyed gradually. For example in petroleum industries, H_2S at high temperature attacks steel forming a FeS scale, which is porous and interferes with normal operations.

4.5.1.3. Liquid metal corrosion

It is due to chemical action of liquid metal flowing through a pipe made of another solid metal or alloy at high temperatures. The corrosion reaction involves the dissolution of a solid metal by a liquid metal or the penetration of liquid metal into the solid metal causing corrosion of solid metal. Such corrosion occurs in devices used for nuclear power.

4.5.2 Electrochemical or Wet Corrosion

This type of corrosion occurs when

(i) a conducting liquid is in contact with metal

(ii) when two dissimilar metals or alloys in contact with a solution.

This corrosion forms separate anodic and cathodic areas through which corrosion current flows in conducting solution. The electrons are liberated by **redox process** in which **oxidation occurs at the anode and the reduction occurs at the cathode**. At anodic area, liberation of free

electrons takes place with dissolution of anodic metal. **Hence, corrosion always occurs at anode.**

At anode: M (Metal) → M^{n+} (Metal ion) + ne^- (Oxidation)

M^{n+} (Metal ion) → Dissolves in solution.
↳ Forms compounds

At cathodic areas, gain of electrons takes place by forming some ions like OH^-, O^{2-}

The metallic ions from anode and non-metallic ions from cathode diffuse towards each other through conducting medium and form a corrosion product between anode and cathode. The electrons set free at the anode flow through the metal and are finally consumed in the cathodic reaction. Thus, the electrochemical corrosion involves

- the formation of anodic and cathodic areas or parts
- presence of a conducting medium,
- anodic disolution
- cathodic reduction with formation of corrosion products

Based on the corrosive medium, the cathodic reaction consumes electrons by two ways (i) evolution of hydrogen (ii) absorption of oxygen,

4.5.2.1 Evolution of hydrogen-type

This type of corrosion occurs in acidic environments with the liberation of electrons. For example consider the dissolution of Fe in acidic medium.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(Oxidation)}$$

These electrons flow through the metal, from anode to cathode, where H^+ ions of acidic solution are liberated as hydrogen gas.

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad \text{(Reduction)}$$

The overall reaction is: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$

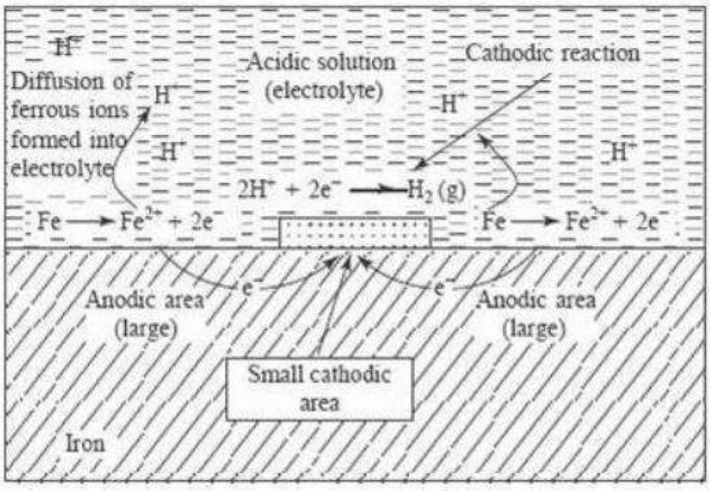


Figure 4.1 Evolution of Hydrogen

Thus the corrosion causes displacement of hydrogen ions from the acidic solution by metal ions. Consequently, all metals ions lying above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

4.5.2.2 Absorption of oxygen type:

Rusting of iron in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen is an example of this type of corrosion. Iron forms a thin surface film due to atmospheric oxidation which can be easily peeled off. The iron exposed part due to peeling serves as anode and oxide part of iron behaves as cathode. The working of formed cell is effected in presence of moisture or in aqueous condition. At the **anodic areas** of the iron dissolves as ferrous ions with liberation of electrons

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(Oxidation)}$$

The liberated electrons flow from anodic to cathodic areas through iron metal and electrons are accepted by the dissolved oxygen present in water

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\,OH^- \quad \text{(Reduction)}$$

The formed Fe^{2+} ions and OH^- ions diffuse and then precipitate ferrous hydroxide as corrosion product

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$$

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide and then to $Fe_2O_3.H_2O$ called yellow rust.

$$4\,Fe(OH)_2 + O_2 + 2\,H_2O \rightarrow 4\,Fe(OH)_3$$

NOTE

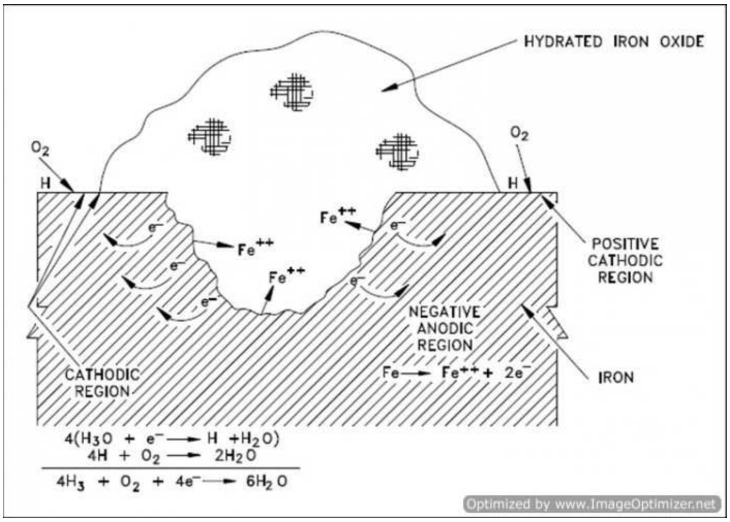


Figure 4.2 Oxygen Absorption Type

If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4.Apart from above discussed classifications, corrosion is also studied as high temperature corrosion and low temperature corrosion.

4.6 Corrosion Kinetics

The electrochemical kinetics of a corrosion reaction depends on the electrode potential, which alters due to the flow of electrons between metal and electrolyte interface. The rate of a redox reaction is zero for an electrochemical system at equilibrium. Hence, the electrochemical kinetics of a corroding metal can be studied by altering the equilibrium by the passage of external voltage through the working electrode which gives parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr})and Tafel slopes (b_a and b_c) which can be obtained from polarization curve, plotted between E and log i. Evaluation of these parameters leads to the determination of corrosion rate. This deviation from equilibrium potential is called polarization. The magnitude of polarization is usually measured in terms of overvoltage which was introduced by Nernst and Caspari. This polarization is said to be anodic, when the anodic processes on the electrode are accelerated by changing the potential in the positive (noble) direction and cathodic, when the cathodic processes are accelerated by changing the potential in the negative (active) direction.

4.7 Pourbaix Diagram For Fe - H_2O System

In a corrosion cell, the electrochemical reactions take place according to the principles of thermodynamics. Thermodynamic changes such as entropy change (ΔS), enthalpy change (ΔH) and free energy change (ΔG) can be determined theoretically using the electrochemical corrosion cell, provided the chemical potentials of reacting species are

known. Experimentally the thermodynamic changes are followed by measuring the corrosion potential. One such an effort was given by Pourbaix who correlated potential (E) with pH to study the thermodynamic behavior of a metal and associated species in given environmental conditions. Hence E-pH diagrams are typically plotted for various equilibria on normal cartesian coordinates with potential (E) as the ordinate and pH as the abscissa as shown in Fig.1.1 called Pourbaix diagram. Potential-pH diagrams are called as Pourbaix diagrams named after its originator, Pourbaix (1963) a Belgium electrochemist and corrosion scientist. These diagrams represent the stability of a metal as a function of potential and pH. At a particular combination of pH and potential, a stable phase can be determined from the Pourbaix diagram. In such diagrams, the redox potential of the corroding system is plotted on a vertical axis and the pH on a horizontal axis. These diagrams are constructed from calculations based on Nernst equations and solubility data for metal and its species, such as Fe, Fe_2O_3, $Fe(OH)_2$ and Fe_3O_4 in equilibrium.

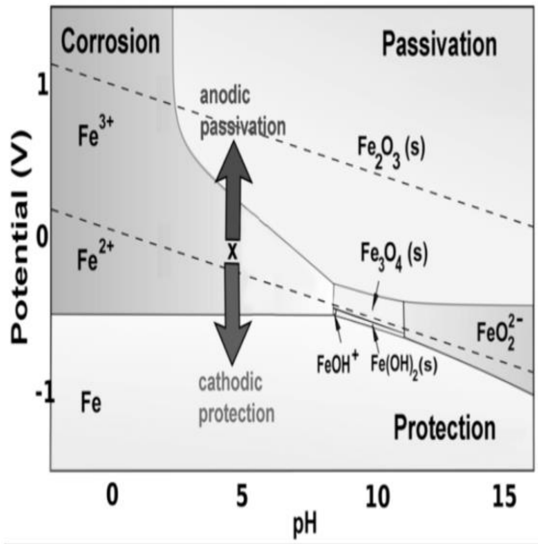


Figure 4.3 Pourbaix Diagram

4.7.1 Characteristics of a Pourbaix Diagram

- pH is plotted on the horizontal axis and redox potential (E) as against SHE on the horizontal axis.
- The horizontal lines represent electron transfer reactions. They are pH independent but are potential dependent. These lines separate the regions of stability, e.g. Fe and Fe^{2+} in a potential-pH diagram for $Fe-H_2O$ system.
- The vertical lines are potential independent but pH dependent and not accompanied by any electron transfer, e.g. lines corresponding to the following reactions:

NOTE

$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$

$Fe^{3+} + 3H_20 \rightleftharpoons Fe(OH)_3 + 3H^+$

- The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. These equilibria indicate electron transfer as well as pH, e.g.

  $Fe_20_3 + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3H_20$

  The above reaction indicates both electron transfer and pH change.
- The concentration of all metal ions is assumed to be 10^{-6} mol per liter of solution. At lower concentration, corrosion should not occur.
- The diagram is computed for the equilibrium conditions at 25°C.
- The upper end of the redox potential axis is the noble end and the lower end, the active end, meaning that the oxidizing power increase with increasing potential.

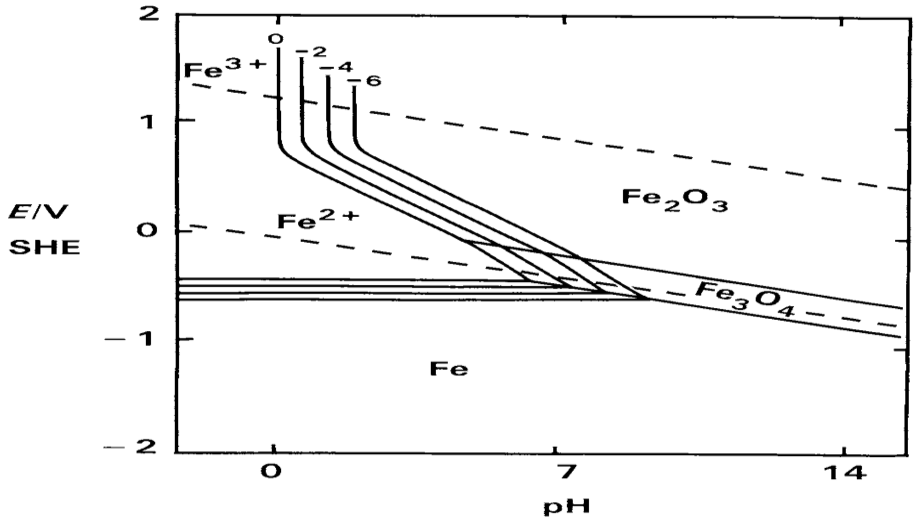


Figure 4.4 Pourbaix diagram for iron water system

The diagram shows all possible equilibria between various ions of iron and water together with their nature and activities. It shows the directions of the various reactions at a given pH and potential in addition to estimating the composition of corrosion products at various pH and potentials. Further this diagram predicts the pH and potential at which the corrosion is reduced.

4.7.2 Limitation of Pourbaix diagram

Though Pourbaix diagrams provide a large volume of thermodynamic data in an efficient and compact format, they remain

silent about the kinetic aspects of corrosion process. Further they do not deal with the effect of impurities or alloying elements present in the metal, variation of electrode potential with time, velocity and temperature changes occurring under experimental conditions.

4.8 Passivity

Passivity or passivation is the phenomenon in which a metal or an alloy exhibits a much higher corrosion-resistance than expected from its position in the electrochemical series. Passivity is the result of the formation of a highly protective, but very thin and invisible film on the surface of metal or an alloy, which makes it more noble. This film is insoluble, non-porous and of such a self-healing nature. Examples of passive metals and alloys are Ti, Al, Cr, and a wide variety of stainless steel alloys, containing Cr. They exhibit outstanding corrosion resistance in oxidising environments and becomes chemical active in reducing environments. The passivity of certain metals in aerated 0.5 M NaCl solution falls in the following order

$$Ti \rightarrow Al \rightarrow Cr \rightarrow Be \rightarrow Mo \rightarrow Mg \rightarrow Ni \rightarrow Co \rightarrow Fe \rightarrow Mn \rightarrow Zn \rightarrow Cd \rightarrow Sn \rightarrow Pb \rightarrow Cu.$$

The metals exhibit its passivity character only in certain environment condition and tend to maintain thin surface protective oxide films. The oxide film on damage is automatically repaired by available atmospheric oxygen and becomes chemically active and is rapidly corroded in deoxygenated environments. For example, the austentic stainless steels are quite good resistant to the action of aerated dilute sulphuric acid, but show low resistance in air-free acid. The action of concentrated HNO_3 on active metals produces a thin protective oxide film and making them passive. This is particularly remarkable in Al, which although very active chemically is not attacked by strongly concentrated nitric acid. On the other hand, dilute nitric acid on Fe stimulates the cathodic reactions and hence rapid corrosion of iron can occur without hydrogen gas evolution. In case of stainless steels and titanium, the protective oxide film is maintained, even in dilute HNO_3 so that these exhibit high corrosion-resistance in HNO_3 solution over a wide range of concentrations.

4.8.1 Conditions for Passivation

Transition metals such as Fe, Cr, Ni and Ti exhibit an active-passive behavior in aqueous solutions. A metal exposed to an aqueous solution is said to be corroded, if its electrode potential is increased with increase of current density. The maximum current density associated with the dissolution process indicates the extent of corrosion. But during the corrosion process the current density is drastically reduced at one

NOTE

particular point and the metal is passivated. The passiveness of metal is due to the formation of thick surface protective film. Iron shows passivity in acids containing SO^{2-}, $NO^{-}CrO^{2-}$, etc. Such metals are called active passive metals. The above metals exhibit S-shaped polarization curves which are characteristic of metals. The above metals show a transition from an active state to a passive state and passivity occurs when the corrosion potential becomes more positive than the equilibrium potential of the metal and its metal oxide.

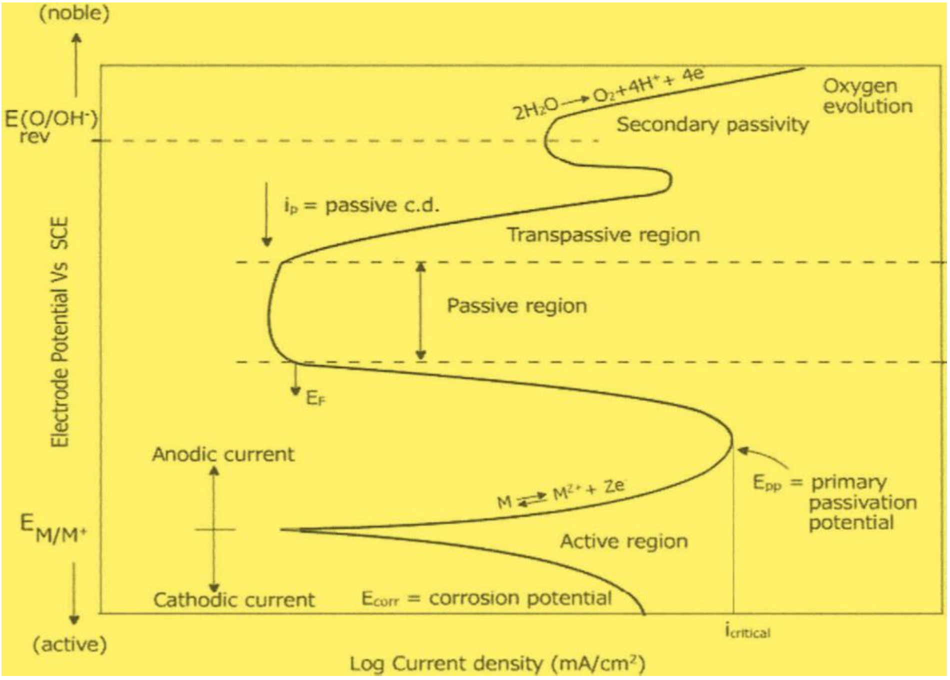


Figure 4.5 Passivity Diagram

The anodic dissolution behavior of a metal demonstrate an active-passive behavior as shown in Figure 4.4 Let the reversible potential of a hypothetical metal M is designated by E (M / M^{2+}) and that of oxygen be E_{rev} (0). The anodic and cathodic polarization curves in the active region intersect at the corrosion potential (E_{Corr}). The anodic curve shows a Tafel behavior with a slope as b_a. Similarly, the cathodic curve is obtained by deviation from E_{Corr} in the active direction and the cathodic Tafel slope is given as b_c. On polarizing the metal in the noble direction from E_{Corr} it is observed that as the potential increases, the rate of dissolution of the metal also increases. The highest rate of corrosion is achieved at a maximum current density, called critical current density ($i_{critical}$). The lower portion of the anodic curve (nose of the curve) exhibits a Tafel relationship up to $i_{critical}$ which can be considered as the current required to generate sufficiently high concentration of metal cations such that the nucleation and growth of the surface firm can proceed. The potential corresponding to $i_{critical}$ is called the *primary passive potential* (E_{pp}) as it represents the transition of a metal from an active state to a passive state. Because of the onset of passivity, the current density (log *i)* starts to decrease beyond E_{pp} due to the oxide film

formation on the metal surface. Beyond E_{pp} the current continues to decrease until at a certain value of potential, it drops to a value orders of magnitude lower than $i_{critical}$. The potential at which the current becomes virtually independent of potential and remains virtually stationary is called the *flade potential* (E_F). It represents the onset of full passivity on the metal surface due to film formation. The minimum current density required to maintain the metal in a passive state is called *passive current density* (i_p). On proceeding further transpassive region is noticed.

4.9 Check Your Progress Questions

1. Define Corrosion
2. Write the difference between electro chemical series and galvanic series?
3. Describe the classification of Chemical corrosion
4. Dicuss about the limitation of pourbaixdiagram

4.10 Answers to Check Your Progress Questions

1. It is process of deterioration or destruction metallic surface with consequent loss of a solid metallic material, through a chemical or electrochemical attack by its environment is called as corrosion. Corrosion is a "**reverse process of extractive metallurgy**".

Electrochemical series	Galvanic series
Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration.	The series was developed by studying corrosion of metals and alloys in unpolluted sea-water without their oxide films
The position of given element is fixed	The position of a given metal may shift
The series comprises of metals and non-metals.	The series comprises of metals and alloys.

3. Chemical corrosion are further classified as:

1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

4. Though Pourbaix diagrams provide a large volume of thermodynamic data in an efficient and compact format, they remain silent about the kinetic aspects of corrosion process. Further they do not deal with the

NOTE

effect of impurities or alloying elements present in the metal, variation of electrode potential with time, velocity and temperature changes occurring under experimental conditions.

4.11 Summary

- The process of deterioration or destruction metallic surface with consequent loss of a solid metallic material, through a chemical or electrochemical attack by its environment is called as corrosion.
- The corrosion processes are classified as chemical and electrochemical type.
- The process of corrosion is slow and occurs only at surfaces of metals.But the losses resulted due to corrosion processes are enormous which are visualized as destruction of machines, equipment and different types of structural damages.
- The corrosion processes are classified as chemical and electrochemical type.
- Passivity or passivation is the phenomenon in which a metal or an alloy exhibits a much higher corrosion-resistance than expected from its position in the electrochemical series.

4.12 Keywords

Corrosion is a reverse process of extractive metallurgy.

Electro Chemical Series: The arrangement of standard reduction electrode potential of elements inthe increasing order is called as electrochemical series .

Galvanic series was developed by studying corrosion of metals and alloys in unpolluted sea-water without their oxide films.

Nernst and Caspari introduced by The magnitude of polarization is usually measured in terms of overvoltage.

Pourbaix diagram: The stability of a metal as a function of potentialand pH. At a particularcombination of pH and potential, a stable phasecan be determined from the Pourbaix diagram.

Passivity: is the result of the formation of a highly protective, but very thin and invisible film on the surface of metal or an alloy, which makes it more noble.

4.13 Self-Assessment Questions and Exercises

1. Discuss about the oxidation corrosion
2. Write the corrosion products during hydrogen type of corrosion.
3. Discuss about the pourbaix diagram for Fe-H_2O system.

4. What is meant by passive state of a metal?
5. Write a note on condition of passivitation

NOTES

4.14 Further Readings

1. D. Jones - Principles and prevention of corrosion, Macmillan Publications New York, (1992).
2. J.J. Meketta - Cathodic Protection Theory and practice, Marcel Dekker Publication, New York, (1993).
3. S.N. Banerjee - An introduction to corrosion and corrosion inhibition, Oxonian Press Ltd., New Delhi.
4. L.L. Shrier - Corrosion Vol I & II Goege Nouns Ltd., Southampton Street, London.
5. M G Fontana & N D Greene, Corrosion Science and Engineering. McGraw Hill Book Co., New York.

Unit -5: Methods of Corrosion Structure

Structure

5.0 Introduction

Corrosion is chemical or electrochemical process which acts reverse of metallurgical process. In accordance with the thermodynamically drive, world is facing huge economic losses due to corrosion. Mostly many engineering structures encounters corrosion damages constituting material cost and fabrication charges. To combat the same, a keen knowledge about the various corrosion processes has to be studied. The factors inducing corrosion and supporting environments are studied thoroughly. Using the gained information corrosion kinetic phenomena are learned to access the rate of corrosion. The obtained rate is properly correlated and control measures are triggered.

5.1 Objective

Aftergoing through this unit, you are able to

- understand the various types of corrosion process
- access the extent of corrosion damage
- gain knowledge about the corrosion kinetic phenomena.

5.2 High-Temperature Corrosion

High-temperature corrosion is a form of corrosion that does not require the presence of a liquid electrolyte. It is also called as called *dry corrosion* or *scaling.* High-temperature oxidation of metals and alloys are regarded as high-temperature corrosion. In most industrial environments, oxidation process takes part in the high-temperature corrosion reactions. Alloys often undergo oxidation reaction to develop a protective scale such as sulfidation, carburization, and other forms of high temperature products to resist corrosion attack. The names of the high temperature corrosion mechanisms are determined by the formed corrosion products. For example, oxidation implies oxides, sulfidation implies sulfides, sulfidation /oxidation implies sulfides plus oxides, and carburization implies carbides. The properties of high-temperature oxide films, such as thermodynamic stability, ionic defect structure, and detailed morphology play a crucial role in determining the oxidation resistance of a metal or alloy in a specific environment. High-temperature corrosion is a widespread problem in various industries such as

- Power generation
- Aerospace and gas turbine
- Heat treating
- Mineral and metallurgical processing
- Chemical processing
- Refining and petrochemical
- Automotive
- Pulp and paper
- Waste incineration

The determination of conditions under which a given corrosion product is likely to form under high temperature corrosion is studied under the view of thermodynamics and extent of corrosion damage is accounted by kinetic principles.

5.2.1 Thermodynamics of High Temperature Corrosion

The extent of corrosion caused on metal by oxygen is studied in the light of Ellingham diagram and Vapour species diagram.

5.2.1.1 Ellingham Diagram

The relative stability of metals and their oxidized products are visualized by Ellingham diagrams in which standard free energy of reaction (ΔG^0) is plotted against temperature. The values in ΔG^0 on an Ellingham diagram (Figure. 5.1) are expressed as kilojoules per mole of O_2 to normalize the scale and are able to compare the stability of these oxides directly. For a given reaction, activities of M and MO_2 are taken

NOTE

as unity and are used to express the oxygen partial pressure at which the metal and oxide coexist

$$\log p_{O_2} = \Delta G^0 / RT$$

The values of log p_{O_2} is obtained directly from the Ellingham diagram by drawing a straight line from the origin marked O through the free-energy line at the temperature of interest and reading the oxygen pressure from its intersection with the scale at the right side labeled log p_{O_2} Thus from the knowledge of p_{O_2} the extent of oxygen attack for high temperature corrosion can be calculated.

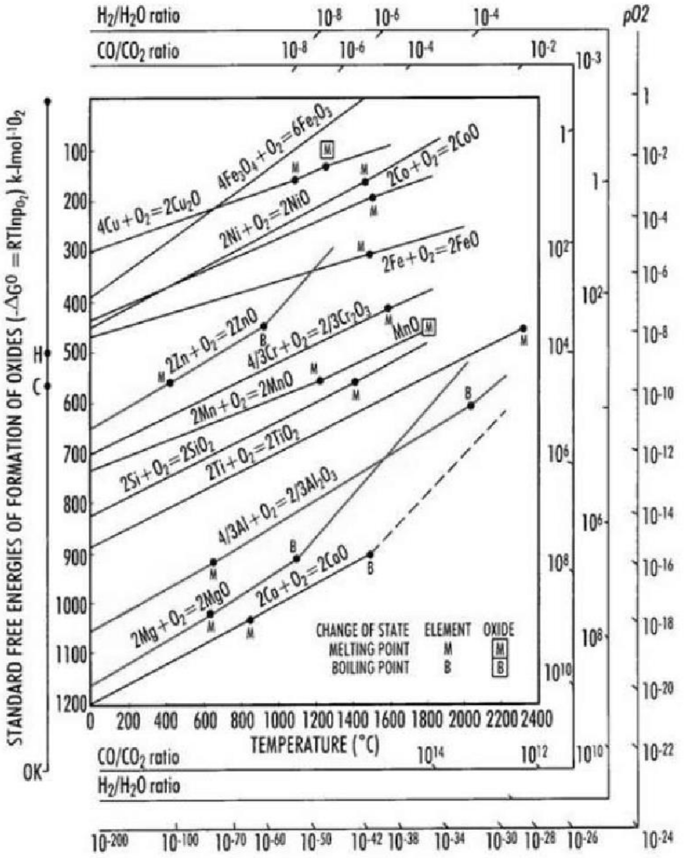


Figure 5.1 Ellingham Diagram

5.2.1.2 Vapour Species Diagrams

Vapour species which are formed in the corrosive environment have a strong influence over rate of high temperature corrosion process and the rate is governed by the nature of volatile corrosion products. Gulbransen and Jansson have shown that metal and volatile oxide species are important in the kinetics of high-temperature oxidation of carbon, silicon, molybdenum, and chromium. Generally, six types of oxidation phenomena are identified during high temperature process. They are

1. At low temperature, diffusion of oxygen and metal species through a compact oxide film
occurs

2. At moderate and high temperatures, a combination of oxide film formation and oxide volatility happens
3. At moderate and high temperatures, transport of oxygen through the oxide lattice and mechanical cracks occurs
4. At moderate and high temperatures, the direct formation of volatile oxide gases is visualized
5. At high temperature, the gaseous diffusion of oxygen through a barrier layer of volatilized Oxides happens
6. At high temperature, spalling of metal and oxide particles are also resulted.

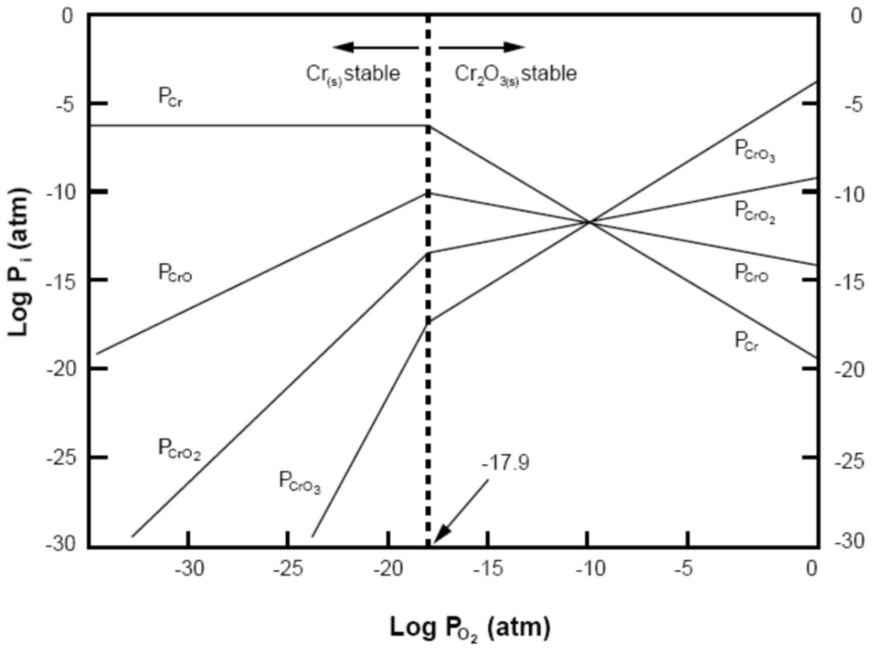


Figure 5.2 Vapour phase equillibrium between chromium and oxygen at 1250^{O}C

From the above diagram partial pressure of oxygen is calculated from which the stability chromium and oxide of chromium is understood.

5.2.2 Kinetics of High Temperature Corrosion

Thermodynamical data concludes about the extent of corrosion attack on metal surface at various temperatures but remains silent about the time period of damage. The first step in high temperature oxidation is the adsorption of oxygen on the surface of the metal, followed by oxide nucleation and the growth of the oxide nuclei into a continuous oxide film covering the metal substrate. The formed film may be protective and nonporous or non-protective and porous as decided by Pilling-Bedworth rule and micro structures of the oxide layer.

5.2.2.1 Pilling-Bedworth Rule

NOTE

The volume of the oxide formed and volume of the metal consumed are important parameter in predicting the degree of protection provided by the oxide scale. The relative correlation between the two is provided by Pilling-Bedworth rule. The rule states that if the oxide volume is relatively low, tensile stresses can crack the oxide layers or if the oxide volume is very high, stresses will be set up and that can also lead to a break in the adhesion between the metal and oxide. Thus for a high degree of protection the volume of the oxide formed should be similar to that of the metal consumed.

Bedworth ratio is given as

$$PB = \frac{\text{Volume of oxide formed}}{\text{Volume of metal consumed}}$$

$$= \frac{Wd}{nDw}$$

where

W- Molecular weight of oxide

D - Density of the oxide

n - Number of metal atoms in the oxide molecule

d - Density of the metal

w - Atomic weight of the metal

PB ratios slightly greater than 1 is expected to indicate optimal protection, with modest compressive stresses generated in the oxide layer.

5.2.2.2 Oxide Microstructures and Rate Laws

The extent of corrosion damage is also influenced by the micro structure of the formed oxide layer. The defect in the sub structures of metal and oxygen will accelerate or retard corrosion. The defects may permit or hinder further oxygen diffusion rate into the oxide layer and making the layer as film or scale. The noticed defects in the oxide layer are classified as p-type and n-type. Thus the rate of diffusion of oxygen governing high temperature corrosion process is studied using rate laws.

5.2.2.2.1 Parabolic rate law.

The parabolic rate law assumes that the diffusion of metal cations or oxygen anions is the rate controlling step and is derived from Fick's first law of diffusion. The concentrations of diffusing species at the oxide-metal and oxide-gas interfaces are assumed to be constant. The diffusivity of the oxide layer is also assumed to be invariant. This assumption implies that the oxide layer has to be uniform, continuous, and of the single phase type which rarely valid. The rate constant, kp changes with temperature as according to an Arrhenius-type relationship.

$$x^2 = k_p t + x_0$$

where x = oxide film thickness

t = time

k_p = the rate constant

x_0 = constant

5.2.2.2.2 Logarithmic rate law

The logarithmic rate law is a following empirical relationship, which has no fundamental underlying mechanism. This law is mainly applicable to thin oxide layers formed at relatively low temperatures and therefore is rarely applicable to high-temperature engineering problems.

$$x = k_e \log (ct + b)$$

where k_e is the rate constant and c and b are constants.

5.2.2.2.3 Linear rate law and catastrophic oxidation.

The linear rate law is also an empirical relationship that is applicable to the formation and
buildup of a nonprotective oxide layer.

$$x = k_L t$$

where *kL* is the rate constant.

5.2.3 High-Temperature Corrosion Problems

The various high temperature corrosion problems visualized in industrial atmosphere are accounted here.

5.2.3.1 Oxidation

Oxidation is generally described as the most commonly encountered form of high-temperature corrosion. However, the oxidation process itself is not always detrimental. In fact, most corrosion and heat resistant alloys rely on the formation of an oxide film to provide corrosion resistance. Chromium oxide (Cr2O3, chromia) is the most common of such films. In many industrial corrosion problems, oxidation does not occur in isolation; rather a combination of high-temperature corrosion mechanisms causes material degradation when contaminants (sulfur, chlorine, vanadium, etc.) are present in the atmosphere.

5.2.3.2 Sulfidation

Sulfidation is a common high-temperature corrosion-failure mechanism. It is due to the contamination by sulfur compounds. When examining this form of damage microscopically,
sulpurs often seems to penetrate into the affected alloy as localized pitting attack. Sulfidation are generally induced by H_2S gas in industrial environments.

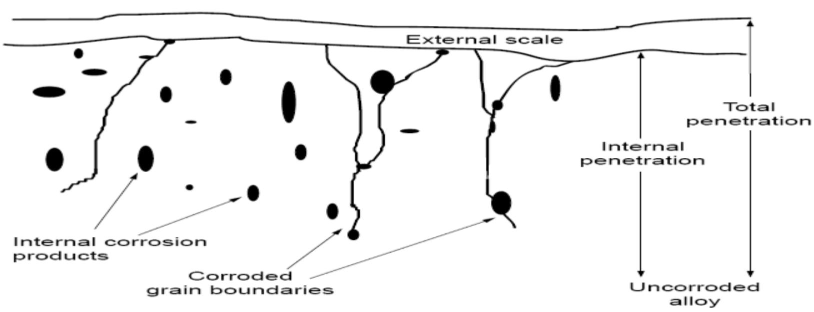


Figure 5.3 Sulphur pitting attack on grain boundaries

NOTE

5.2.3.3 Carburization

Carburization can occur when metals are exposed to carbon monoxide, methane, ethane, or other hydrocarbons at elevated temperatures. Carbon from the environment combines primarily with chromium but also with any other carbide formers Nb, W, Mo, Ti, etc., present in the alloy to form internal carbides. Carbides formed in the microstructure can be complex in composition and structure and can be found to precipitate on the grain boundaries or inside the grains. The main undesirable effect of carbide formation is embrittlement and reduces ductility at temperatures up to 482 to 538°C. Conversion of chromium in the form of stable chromium-rich carbides during carburization also reduces oxidation resistance.

5.2.3.4 Metal dusting

Metal dusting is related to carburization and has been reported in similar industries. In this form of degradation, the corrosion products appear as fine powders consisting of carbides, oxide and graphite (soot). The morphology of attack can be localized pitting or relatively uniform damage. The underlying alloy may or may not display evidence of carburization in the microstructure. Metal dusting is manifested at lower temperatures than carburization, typically between 425 and 815°C. Maximum rates of metal dusting damage are considered to occur around 650 to 730°C.

5.2.3.5 Nitridation

Nitridation usually occurs when carbon, low-alloy, and stainless steels are exposed to an ammonia-bearing environment at elevated temperatures in the industrial production of ammonia, nitric acid, melamine, and nylon. Nitridation can also result from nitrogen atmospheres, especially under reducing conditions and high temperatures. Nitridation is also noticed when chromium and other elements combine with nitrogen to form embrittling nitrides in the microstructure.

5.2.3.6 Gaseous halogen corrosion

The corrosive effect of halogen on passivating alloys is well known in aqueous media. Chlorides and fluorides also contribute to high-temperature corrosion by interfering with the formation of protective oxides or breaking them down if already formed. The main reason for the reduced corrosion resistance in the presence of halogens is the formation of volatile corrosion products that are non-protective.

5.2.3.7 Fuel ash and salt deposits

In many industrial applications, the surfaces undergoing high temperature corrosion are not clean. The surface deposits of ash and/or salt form on the structures induces corrosion. Chemical reactions between these deposits and the protective surface oxide can lead to destruction of the oxide and rapid corrosive attack. In gas turbines, oxidized sulfur contaminants in fuel and sodium chloride from ingested air (marine atmospheres) tend to react to form sulfates that are

subsequently deposited on surfaces. The presence of sodium sulfate, potassium sulfate, and calcium sulfate together with magnesium chloride in marine environments causes problems in ship compressors.

5.2.3.8 Corrosion by molten salts

Corrosion damage from molten salts can occur in a wide variety of materials and by different mechanisms. It has been pointed out that although many studies have been performed, quantitative data for materials selection and performance prediction are rarely available. Molten salt corrosion is usually applicable to materials retaining the molten salt, as used in heat treating, solar and nuclear energy systems, batteries, fuel cells and extractive metallurgical processes.

5.2.3.9 Corrosion in liquid metals

Corrosion in liquid metals is applicable to metals and alloy processing, metals production, liquid metal coolants in nuclear and solar power generation, other nuclear breeding applications, heat sinks in automotive and aircraft valves, and brazing operations. Corrosion damage to containment materials is usually the concern. The most severe problems arise at high temperatures and aggressive melts. Molten steel is typically regarded as a non-aggressive melt, whereas molten lithium is much more corrosive.

5.3 Forms of Corrosions

Fontana and Greene have conveniently classified the various types of corrosion into eight forms.

The eight forms of corrosion are as follows

(1) Uniform attack (or general corrosion)
(2) Crevice corrosion
(3) Pitting
(4) Stress-corrosion cracking
(5) Galvanic corrosion (two metal corrosion)
(6) Intergranular corrosion
(7) Selective leaching (dealloying)
(8) Erosion corrosion

5.3.1 Uniform Corrosion

Uniform corrosion is one of the major forms of corrosion which are illustrated schematically in Figure 5.4. In uniform corrosion, the metal is attacked more or less evenly over its entire surface. All portions of the metal surface are attacked more uniformly over the entire surface, and the metal piece is thinned away by the process of corrosion until the piece eventually fails. Examples include the corrosion of zinc in hydrochloric acid and the atmospheric corrosion of iron or steel in aggressive outdoor environments. During corrosion localized anodes and cathodes are formed and positions of these localized anodes and cathodes change with time and corrode all over the metal surface so that the overall effect is that the metal is attacked uniformly.

NOTE

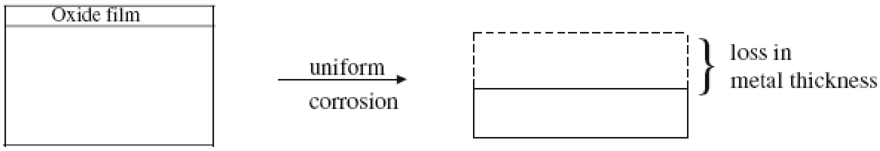


Figure 5.4 Block Diagram

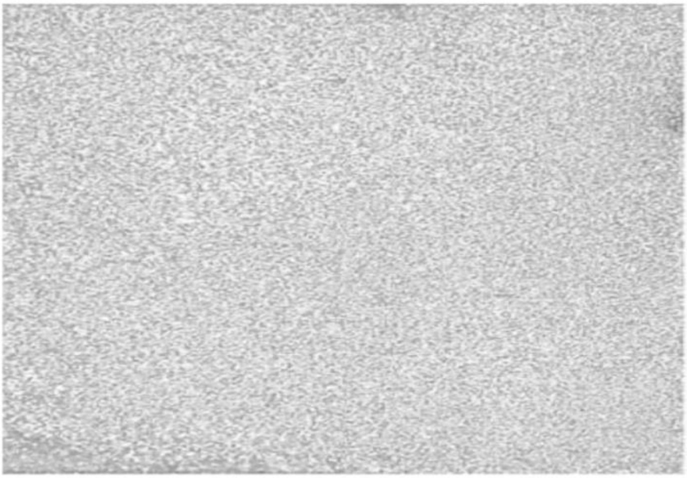


Figure 5.5 Uniform corrosion of Zinc exposed to hydrochloric acid

5.3.2 Crevice Corrosion

The common form of differential aeration or oxygen cells corrosion is called as crevice corrosion. A metal confined within a narrow end experiences a reduced concentration of dissolved oxygen relative to the metal outside the crevice which is exposed to bulk electrolyte. Thus differential oxygen cell makes the metal inside the crevice anodic to the metal outside the crevice and a corrosion cell is formed. This type of corrosion is due to electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations of oxygen or aeration. This results in localized variation in metal-ion concentrations caused by local temperature differences or inadequate agitation or slow diffusion of metal-ions produced by corrosion.

Differential aeration corrosion occurs when one part of metal is exposed to a different air concentration from the other part causing a difference in potential between the two aerated areas. Poorly oxygenated parts serves as anode and more oxygenated areas serve as cathode. Consequently, a differential in concentration corrosion cell is localized in a particular area of material structure causing corrosion damage. Electrons flow from anode towards the cathode and aeration of metal causes a flow of differential current. For e.g., if a metal (say Fe) is partially immersed in a dilute solution of a neutral salt like NaCl and the

solution is not agitated properly then the parts adjacent to the waterline are more strong aerated and hence, become cathodic. On the other hand parts immersed to greater depth show a smaller oxygen concentration and become anodic. Hence a difference in potential is created which causes a flow of current between the two differentially- aerated areas of the same metal. Iron will dissolve at the anodic areas with the liberation of electrons and the liberated electrons are taken by oxygen near the cathode to form hydroxyl ions.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(Oxidation)}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\,OH^- \quad \text{(Reduction)}$$

$$Fe + 1/2\,O_2 + H_2O \rightarrow \underbrace{Fe^{2+} + 2\,OH^-}_{\text{Corrosion products}} \quad \text{(Overall)}$$

The circuit is completed by migration of ions, through the electrolyte, and flow of electrons, through the metal, from anode to cathode. In a similar way, iron also corrodes under drops of water. Areas covered by droplets, having no access of oxygen, become anodic with respect to the other areas, which are freely exposed to air.From the above, it is clear that oxygen concentration cell increases corrosion, but it occurs where the oxygen concentration is lower. A pictorial representation of differential aeration corrosion is depicted in Figure 5.6.

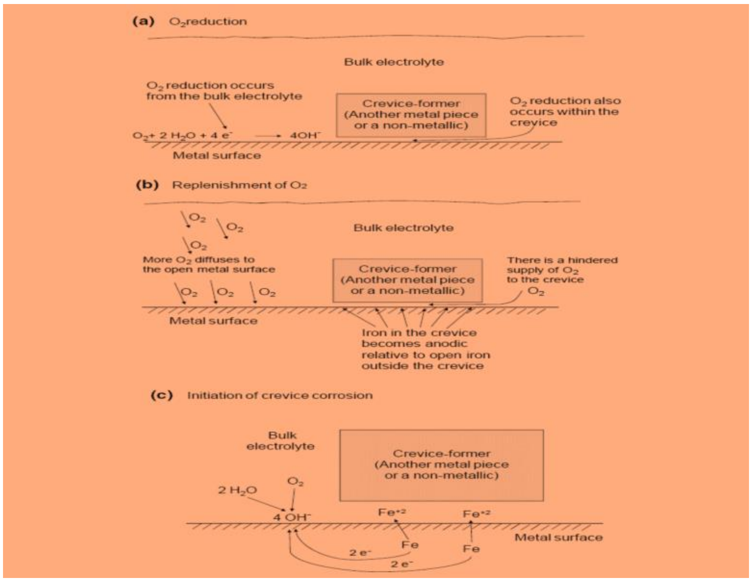


Figure 5.6 Aeration Corrosion

Differential aeration corrosion is accelerated in inaccessible parts of machineries such as cracks or crevices which serve as node for anodic

dissolution. Oxygen concentration corrosion is also noticed under accumulation of dirt sand, scale or other contamination compounds over material structures. The accumulated rust or scale or sand, etc., restricts the access of oxygen and establishes an anode to promote localized corrosion or non-uniform corrosion. Metals exposed to aqueous media under blocks of wood or pieces of glass is an another example for this type of corrosion. The differential aeration type of corrosion is a form of localized attack on some oxygen-deficient areas, resulting in characteristics localized pitting. This attack becomes more intensified with the time, because the corrosion products accumulate around a small anodic area, thereby making inaccessibility of that part more effective.

5.3.3 Pitting Corrosion

Pitting corrosion is a localized form of corrosion attack resulting in the formation of cavities in the dissoluting metal. Pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting is the result of the breakdown or cracking of the protective film on a metal at particular points. This gives rise to the formation of small anodic and large cathodie areas. In proper corrosive environment the formed areas produces corrosion current. Breakdown of the protective film may be caused by

- surface roughness due to ununiformed finish
- scratches or polished edges
- non-uniform stresses
- alternating stresses
- under overloading of engineering structures
- impingement attack
- chemical attack.

Passive layers of metals on above said conditions peeled of from metal surface and propagate pitting corrosion in the exposed areas all conditions. Passivity of metals are destroyed by the process of pitting corrosion. For e.g., stainless steel and aluminium show characteristic pitting in chloride solution. The presence of the extraneous impurities like sand, dust, scale, etc., embedded on the surfaces of metals also lead to pitting corrosion. Owing to the differential amount of oxygen in contact with the metal the small part underneath the impurity become the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion therefore start at underneath the impurity. Once a small pit is formed, the rate of corrosion will be increased.

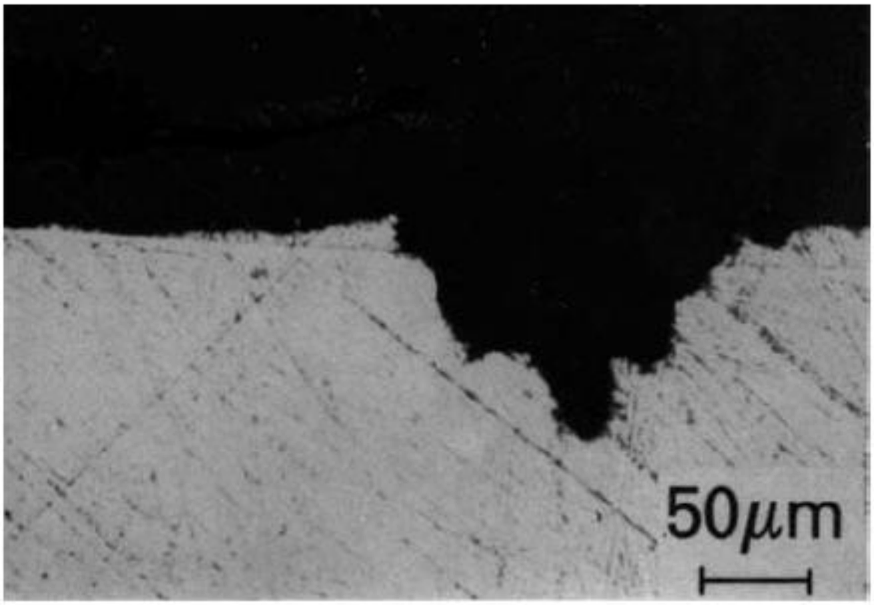


Figure 5.7 Cross sectional view of corrosion pit

5.3.4 Stress Corrosion

Stress corrosion or stress cracking is the combined effect of static tensile stresses and the corrosive environment on a metal. The presence of tensile stress and a specific corrosive environment are necessary for occurrence of stress corrosion. The corrosive agents are caustic alkalis and strong nitrate solution for mild steel, traces of ammonia for brass and acid chloride solution for stainless steel. Corrosive agents are highly specific and selective in nature.This type of corrosion is seen in fabricated articles of certain alloys such as high-zinc brasses and nickel brasses due to the presence of stresses caused by heavy working like rolling, drawing or insufficient annealing. However, pure metals are relatively immune to stress corrosion.

Stress corrosion involves in a localized electrochemical corrosion occurring in narrow paths as anodes unstressed metal surface as cathodes. Presence of stress produces strains resulting in localized zones of higher electrode potential and becomes chemically active for corrosive attack resulting in the formation of a crack which grows and propagates perpendicular to the operating tensile stress in a machineries and results in failure of equipment.Some typical stress corrosion processes are

5.3.4.1 Season cracking

It is noticed in corrosion of copper alloys of brass kind. Pure copper is immune to stress corrosion but presence of small amounts of alloying element like P, As, Sb, Zn, Al, Si result in cracking. Brass

NOTE

undergoes cracking in an atmosphere containing traces of ammonia or amines. The attack occurs along the grain boundaries, which become more anodic with respect to the grain themselves. Cu and Zn present in brass are chemically active in ammonia solutions and results in dissolution of brass with initiation of crevice and propagates progressively.

5.3.4.2 Caustic embrittlement

It is a very dangerous form of stress corrosion occurring in mild steel exposed to alkaline solutions at high temperatures and stresses such as in boilers and heat-transfer equipment in which water of high alkalinity attacks the mild steel plates particularly at the crevices near rivets. The soften boiler waters usually have a certain proportion of sodium carbonate resulted after former's treatment in lime soda process. Those water when introduced into high-pressure boilers undergoes dissolution with the formation of sodium hydroxide (Caustic) and carbon dioxide

$$Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2\uparrow$$

and makes boiler-water alkaline. This very dilute alkaline boiler-water flows into the minute hair-cracks and crevices in boilers due to capillary action. The settled alkaline solution evaporates water and the caustic soda concentration builds up in the hair crack. This concentrated alkali dissolves boiler iron as sodium ferroate causing stress over the metal. The sodium ferroate decomposes into NaOH (regenerated) with precipitation of magnetite (Fe_30_4) and enhances further dissolution of iron.

$$3\ Na_2FeO_2 + 4\ H_2O \rightarrow 6\ NaOH + Fe_3O_4 + H_2$$

or

$$6\ Na_2FeO_2 + 6\ H_2O + O_2 \rightarrow 12\ NaOH + 2\ Fe_3O_4$$

5.3.5 Galvanic (or) Bimetallic Corrosion

When two dissimilar metals such as iron and copper are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called as galvanic corrosion. In Fe-Cu couple, iron is present higher in electrochemical series forms the anode and gets attacked and dissolved whereas copper appears lower in electrochemical series or towards in noble direction to iron acts as cathode. In acidic solution, the corrosion occurs by the hydrogen evolution process while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anodic metal,

NOTES

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(Oxidation)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(Reduction in acidic medium)}$$

(**OR**)

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\,OH^- \quad \text{(Reduction in neutral medium)}$$

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \quad \text{(Overall)}$$

(**OR**)

$$Fe + 1/2\,O_2 + H_2O \rightarrow \underbrace{Fe^{2+} + 2\,OH^-}_{\text{Corrosion products}} \quad \text{(Overall)}$$

Iron to the cathodic metal copper. Thus, it is evident for the above equations that the corrosion occurs at the anodic metal while the cathodic part is protected from the attack. Some of the examples are (i) Steel screws in a brass marine hardware (ii) Load-antimony solder around copper wire (iii) A steel propeller shaft in bronze bearing and (iv) Steel pipe connected to copper plumbing.

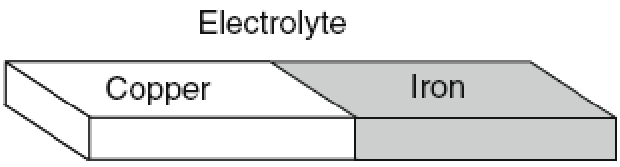


Figure 5.8 Fe-Cu galvanic couple

5.3.6 Intergranular Corrosion

This type of corrosion occurs along grain boundaries of materials sensitive to corrosive attack or corrosive liquid with selective attacking character to attack grain boundaries. During intergranular corrosion process the grain interiors remains unattached or sometimes slightly corroded. This type of corrosion arise due to the fact that the grain boundaries contain material which shows electrode potential more anodic than that of the grain center in the particular corroding medium. This results in the precipitation of certain compounds at the grain boundaries, thereby leaving the solid metal solution just adjacent to the grain boundary depleted in that constituent. The depleted solid solution acts as anode to the grain centres as well as to the precipitate compound and starts deteriorating by the corrosive environment. The grain boundary or inter granular type of corrosion is often noticed in alloys exposed to corrosive environment. For e.g., during the welding of stainless steel which is an alloy of Fe, C and Cr, chromium carbide is precipitated at the grain boundaries and causing the region just adjacent to grain boundaries becomes depleted in chromium composition and behaves anodically with

respect to the solid solution within the grain and to the precipitated particles of the chromium carbide.

Usually, corrosion in welded stainless steel is not a serious problem since corrosion resistance can be restored by a heat-treatment method which dissolves the chromium carbide precipitated during welding. However, when stainless steel assemblies are too large to be heat treated, it is then necessary to prevent the depletion of chromium. Intergranular corrosion follows the path of grain boundaries and occurs on microscopic scale without any apparent external signs of any intensive attack. Hence sudden failure of material structure occurs with huge corrosion damage due to loss of cohesion between grains.

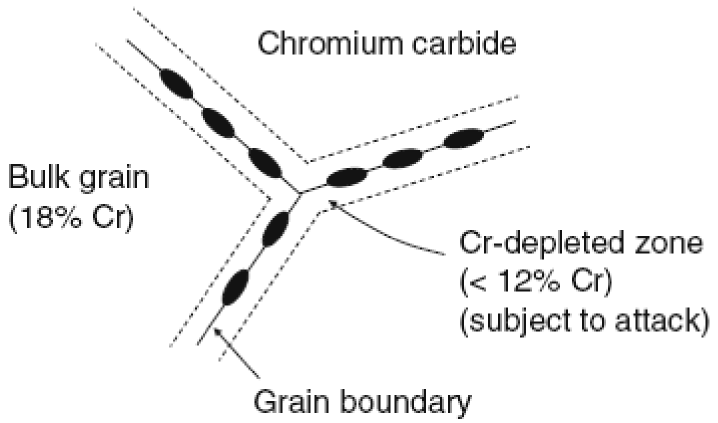


Figure 5.9 Intergranular corrosion as seen during welding of stainless steel alloy

5.3.7 Selective Leaching

Selective leaching or dealloying is the preferential removal of one element by corrosion from a solid alloy. Examples include the selective removal of zinc from copper zinc alloys and the process is known as dezincification and the preferential removal of iron from gray cast iron called graphitic corrosion.

This type of corrosion occurs due to the exposure of materials to a stagnant or slow moving body of water containing higher quantities of O_2 ,CO_2 and chlorides. The quantity of a metal in an alloy also determines susceptibility to preferential attack which is shown in Figure 5.10 For instance, if zinc content in a brass is less than 15% then dezincification does not occur significantly. Dezincification in corrosion environment will occur if the zinc content is higher 15% The rate at which dezincification takes place is also affected by the environmental temperature. The corrosion processs is well noticed at higher temperatures as shown in fig.

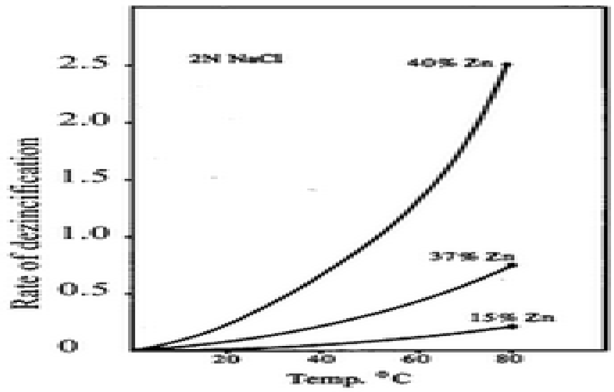


Figure 5.10 Dezincification process

Graphite leaching corrosion in grey cast irons is also a common example of dealloying process. The corrosion forms a galvanic cell in which the graphite becomes cathodic to the anodic iron.

5.3.8 Erosion corrosion

Five more forms of localized corrosion are initiated by the mechanical process over material structures in industries. The five forms are mechanically assisted corrosion are

- Stress-corrosion cracking
- Corrosion fatigue
- Cavitation corrosion
- Erosion corrosion
- Fretting corrosion

The stress corrosion as discussed earlier, rest four forms are accounted thereof in the succeeding sections

5.3.8.1 Corrosion Fatigue

Corrosion fatigue is the cracking of a metal or alloy due to the combined action of a repeated cyclic stress and a corrosive environment. Corrosion fatigue can occur in aircraft wings, in bridges and in offshore platforms which are impacted by ocean waves and in vibrating machinery. In additionstainless steel and titanium alloys used as orthopedic implants can also undergo corrosion fatigue under cyclic stresses in the electrolyte found within the human body.

5.3.8.2 Cavitation Corrosion

Cavitation corrosion is the combined mechanical and corrosion attack caused by the collapse and impingement of vapor bubbles in a liquid near a metal surface. Cavitation corrosion can occur in ship propellers, within pumps, on turbine blades, on hydrofoils, and on other surfaces where there is a high-velocity fluid flow and where pressure changes are encountered.

5.3.8.3 Erosion corrosion & Fretting corrosion

NOTE

Two additional forms of mechanically assisted corrosion are erosion corrosion and fretting corrosion. In erosion corrosion, the mechanical effect is provided by the movement of a corrosive liquid against the metal surface in fretting corrosion, the mechanical effect is due to the abrasive wear of two metal surfaces sliding or vibrating past each other. Erosion corrosion can occur in various types of equipment exposed to fast-moving liquids. These include piping systems, bends, elbows, valves, and pumps. Polymer, glass, and metal surfaces on moving aircraft can be damaged by rainwater erosion. Solids suspended in a liquid can also cause erosion corrosion, as in coal slurry pipelines. Fretting corrosion can occur in loaded interfaces which move past each other, such as in vibrating machinery, connecting rods, or springs. Fretting corrosion can also be a problem with orthopedic implants placed in the human body. Fretting corrosion is also called wear corrosion or tribo corrosion.

5.3.9 Microbiological Corrosion

Apart from the above discussed corrosion forms corrosion caused by the metabolic activity of various micro-organisms on metal surface is called microbiological corrosion. The micro-organisms can develop in an environment with or without oxygen and are classed as aerobic or anaerobic conditions which induces corrosion attack . A brief summary of various organism triggering microbiological corrosion or **microbial induced corrosion (MIC)** or **bio-corrosion** are stated below

(1) Sulphate reducing bacterias are responsible for anaerobic corrosion of iron and steel. Sulphates present in the corrosive environments serves as nourishers in presence of little oxygen. Other optimum conditions for their growth are in the order of 25 to 30°C and pH from 5 to 9. The mechanism of anaerobic microbiological corrosion of iron is:

Anodic solution of iron:

$$8\,H_2O \Longleftrightarrow 8H^+ + 8\,OH^-$$

$$4\,Fe + 8\,H^+ \Longleftrightarrow 4\,Fe^{2+} + 8H$$

Depolarization, due to activity of bacterias:

$$H_2SO_4 + 8H \Longleftrightarrow H_2S + 4\,H_2O$$

Corrosion products:

$$Fe^{2+} + H_2S \Longleftrightarrow FeS + 2\,H^+$$

$$3\,Fe^{2+} + 6\,OH^- \Longleftrightarrow 3\,Fe(OH)_2$$

The principal corrosion products are black iron sulphide and ferrous hydroxide. The corrosion is intense and localized.

(2) Sulphur bacterias are mostly aerobic, and oxidize sulphur present in their cells to sulphuric acid which then attacks the iron. They grow best under acid conditions of pH from 0 to 1.

(3) Iron and manganese micro-organisms are aerobic micro-organisms and| live by taking into their cells iron and manganese ions which they metabolizes in presence of oxygen forming insoluble hydrates of iron and manganese dioxide as corrosion products. Iron bacterias grow in stagnant or running water at 5°C to 40°C and pH between 4 to 10 and with a small amount of free dissolved oxygen.

(4) Film-forming micro-organisms like bacterias, fungi, algae, and diatoms can form microbiological film on an iron surface. Such films are capable of maintaining concentration gradients of dissolved salts, acids and gases on the iron surface thereby leading to the formation of local biological concentration cells and consequent corrosion.

5.4 Chemical and Electrochemical Methods of Corrosion Rate Measurement Methods

5.4.1 Chemical Methods

The kinetics of corrosion processes occurring in aqueous medium are chemically monitored using the following methods.

- Weight loss method.
- Electrical resistance method.
- Gasometric method.

5.4.1.1 Weight loss method (Gravimetric method)

In this method, metal loss due to corrosion is measured by exposing the metal specimen of known composition, area and weight to the corrosive environment for a specified period of time. Then the difference in the weight before and after the exposure (weight loss) is calculated. Care is taken to clean the corroded specimens with the cleaning solutions meant for each metal to remove any corrosion product while measuring the weights. The percentage of inhibition efficiency is calculated from the weight loss studies. Experiments are performed according to a standard method suggested by ASTM G1-90, 1996. Weight-loss methods are slower technique than other techniques but multiple samples can be run simultaneously. This method gives the average corrosion rate over an extended period of time as per the following equation:

NOTE

Corrosion Rate =

$$\frac{\text{Weight loss in g X } 8.76 \text{ X } 10^4}{\text{Alloy density in g/ cm}^3 \text{ X Exposed area in cm}^2 \text{ x Exposed time in h}}$$

5.4.1.2 Electrical resistance method

The electrical resistance (R) of a metal is given by, R = ρ x l/a where R is the resistance, ρ is the specific resistance; l is the length of the specimen and its area of the cross section. Hence, the exposure of the metal (drawn in the form of wire or rod) to the corrosive environment leads to decrease in cross sectional area which increases electrical resistance from which corrosion rates are measured. Major advantage of this method is that the corrosion rate can be measured both in liquid and vapor phases.

5.4.1.3 Gasometric method

This is a reliable and accurate method. Volume of the gas liberated in acid corrosion is measured directly at constant temperature and atmospheric pressure and the metal loss is calculated. Nathen , Hackerman and Mathur *et al* have used this technique and designed gasometric units which were operated under controlled conditions of temperature and pressure. The main disadvantage is that this method cannot be applied to strong oxidizing medium when inhibitors undergo reduction with hydrogen gas evolved and in situations where the stoichiometry of the corrosion reaction is not clearly defined.

5.4.2 Electrochemical methods

Corrosion processes occurring in aqueous medium are generally electrochemical in nature. As stated earlier, the overall reaction is a combination of anodic and cathodic process. The anodic reaction is the dissolution of the metal and the cathodic reaction is the evolution of hydrogen or reduction of oxygen. Highly accurate results are obtained in a short duration of time making use of electrochemical methods. The non- electrochemical methods are time consuming method. Electrochemical methods include direct current and alternating current techniques advocated by Mansfeld and Lorenz for determination of corrosion in the systems, following simple kinetics. Some of the methods are as follows.

5.4.2.1 Tafel extrapolation method

The variation of current with potential of a corroding electrode is analyzed by a plot of η vs log i whose slopes gives the Tafel constants (b_a or b_c) and the intercept gives the corrosion current. At high over potentials the rate expression is,

$$\log i = \log i_{Corr} + \frac{E - E_{Corr}}{b_c}$$

The corrosion rate in mmpy is calculated using the i_{corr} values

$$\text{Corrosion rate} = 3.2 \text{ x } i_{Corr} (mA/cm^2) \text{ x } \frac{\text{equivalent mass}}{\text{density}}$$

The main disadvantages of this method are

a) large number of measurements are to be made to obtain the data for each curve.
b) the Tafel region gets distorted for systems having more than one cathodic reaction.
c) the method requires a good conducting medium to operate.
d) this method is applicable for those reactions which are activation controlled.

5.4.2.2 Linear polarization method.

Stern & Geary have shown that there is a linear relationship between current and potential when $\eta < 20$ mV. On measuring the slope of E vs i plot, the corrosion current for activation controlled anodic and cathodic reaction can be obtained from the following relationship.

$$\frac{\Delta E}{\Delta i} = \frac{b_a b_c}{2.3(b_a + b_c) i_{corr}}$$

For an anodic activation controlled and cathodic diffusion controlled reaction, the following relationship holds good.

$$\frac{\Delta E}{\Delta i} = \frac{b_a}{2.3 i_{corr}}$$

The term $\Delta E / \Delta i$ have dimensions and hence this technique is also known as polarization resistance method. Even low corrosion rates can be followed with accuracy. But this method requires conducting liquid as a medium.

The main advantages of this method are

a) corrosion rate can be measured even if rapid corrosion occurs.
b) perturbation of corroding specimen is small.
c) even low corrosion rate can be measured accurately.

The disadvantages are

a) the metal should be conducting
b) hysterisis effects are observed in the polarization curves affecting the polarization resistance values (R_p

NOTE

c) this technique can be applied only to systems exhibiting uniform corrosion.

5.4.2.3 Impedance method

Among various a.c. techniques, the impedance technique is widely used due to the main advantage that the double layer capacitance and charge transfer resistance can be determined. The terms resistance and impedance imply a restriction to the current flow. When dealing with d.c., only resistors produce this effect but in the case of a.c. both inductors and capacitors influence electron flow. The circuit diagram for stimulated metal / solution interface is presented in Figure 5.11.

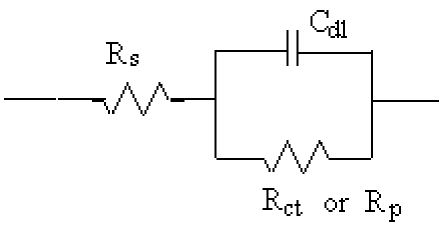


Figure 5.11 Equivalent circuit for impedance analysis

The term C_{dl} in the above figure refers to double layer capacitance, R_s is solution resistance and R_{ct} denotes charge transfer resistance. For the determination of R_{ct} a sinusoidal current (or potential) perturbation of very small amplitude (~10 mV) is applied as a function of frequency. The impedance of the corroding system for various frequencies can be measured using frequency response analyzer. The plot of Z" vs Z' (Nyquist plot) gives R_{ct} values. From R_{ct} the corrosion current can be calculated using Stern – Geary equation as follows.

$$R_{ct} = \frac{b_a \times b_c}{2.3\,(b_a + b_c)\; i_{corr}}$$

To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z''_{max}$) is found out and C_{dl} values are obtained from the following equation.

$$f(-Z_{max}) = \frac{1}{2\pi C_{dl} R_{ct}}$$

The advantages of this method are

a) AC impedance involves measurement of both capacitance and charge transfer resistance. Hence this technique is more valuable.

b) this technique uses amplitudes which are in the range of 5 – 10 mV peak to peak. Hence the perturbation is minimum and reduces the errors caused by the measurement.

c) this method does not involve potential scan and therefore can be applied to low conductivity media also. The impedance of the

corroding system at various frequencies can be measured using lock amplifiers for high frequencies and fast Fourier transform technique for low frequencies.

Other methods such as coulostatic and Faradaic distortion methods have also been developed for the measurement of corrosion rates.

5.4.2.4 Activation polarization

The relation between current and potential for a corroding system can be derived from electrochemical kinetic theory in which the anodic reaction is metal dissolution reaction and the cathodic reaction is hydrogen evolution reaction. General equations for anodic and cathodic reactions are given by equations as below

$$M \rightleftharpoons M^{+} + e$$

$$H^{+} + e \rightleftharpoons H_2$$

The above reactions can be studied using electrochemical methods in which the response of a system to an applied polarization is analyzed. Polarization of an electrode supporting one redox system is given in the Butler-Volmer equation (equation 1.3)

$$i_{reaction} = i_0 \left\{ \exp\left(\beta_{reaction} \frac{nF}{RT} \eta_{reaction} \right) - \exp\left(-\left(1 - \beta_{reaction}\right) \frac{nF}{RT} \eta_{reaction} \right) \right\}$$

where, $i_{reaction}$ - anodic or cathodic current

i_0 - exchange current density

$\beta_{reaction}$ – charge transfer barrier or symmetry coefficient for the anodic or cathodic reaction.

$\eta_{reaction}$ – difference between the equilibrium potential and applied potential (positive for anodic polarization and negative for cathodic polarization)

n - number of participating electrons

R - gas constant

T - absolute temperature

F – Faraday

When $\eta_{reaction}$ is anodic, the second term in the Butler- Volmer equation becomes negligible and i_a can be more simply expressed by equations 1.4, 1.5 and 1.6.

$$i_a = i_0\left[\exp\left(\beta_a \frac{nF}{RT}\eta_a\right)\right]$$

$$\eta_a = b_a \log \frac{i_a}{i_0}$$

$$b_a = 2.3\ \frac{RT}{\beta nF}$$

where i_a is the anodic current, b_a is the Tafel coefficient obtained from the slope of plot between η and log i, with the intercept as i_o.

Similarly for cathodic reaction is expressed as

$$i_c = i_0\left[-\exp\left(-(1-\beta_c)\frac{nF}{RT}\eta_c\right)\right]$$

$$\eta_c = b_c \log\left(\frac{i_c}{i_0}\right)$$

$$b_c = -2.3\ \frac{RT}{\beta nF}$$

where b_C is Tafel constant.

5.4.2.5 Concentration polarization

The corrosion in neutral media consists of metal dissolution as well as oxygen reduction. In such a case the cathodic reaction is purely diffusion controlled which is given as

$$i_c = i_L = -nFD_0\frac{C_{0,bulk}}{\delta}$$

where i_L – limiting current; D_o – diffusion coefficient of species $_O$; $C_{O,bulk}$ – concentration of species O in bulk of the solution and δ – diffusion coefficient.

5.5 Check your progress Questions

1. What is meant by high temperature corrosion
2. State the Pilling-Bedworth rule.
3. Explain the various types of corrosion forms.
4. How galvanic corrosion cell is formed?
5. Account on the various types of mechanical assisted corrosion.

5.6 Answers to Check Your Progress Questions

1. High-temperature corrosion is a form of corrosion that does not require the presence of a liquid electrolyte. It is also called as called *dry corrosion* or *scaling.*

2. The volume of the oxide formed and volume of the metal consumed are important parameter in predicting the degree of protection provided by the oxide scale. The relative correlation between the two is provided by Pilling-Bedworth rule.

3. Fontana and Greene have conveniently classified the various types of corrosion into eight forms.

The eight forms of corrosion are as follows

(1) Uniform attack (or general corrosion)
(2) Crevice corrosion
(3) Pitting
(4) Stress-corrosion cracking
(5) Galvanic corrosion (two metal corrosion)
(6) Intergranular corrosion
(7) Selective leaching (dealloying)
(8) Erosion corrosion

4.When two dissimilar metals such as iron and copper are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called as galvanic corrosion.

5. The five forms are mechanically assisted corrosion are

- Stress-corrosion cracking
- Corrosion fatigue
- Cavitation corrosion
- Erosion corrosion
- Fretting corrosion

5.7 Summary

- Corrosion is chemical or electrochemical process which acts reverse of metallurgical process. In accordance with the thermodynamically drive, world is facing huge economic losses due to corrosion. Mostly many engineering structures encounters corrosion damages constituting material cost and fabrication.
- High-temperature oxidation of metals and alloys are regarded as high-temperature corrosion. In most industrial environments, oxidation process takes part in the high-temperature corrosion reactions.
- The extent of corrosion caused on metal by oxygen is studied in the light of Ellingham diagram and Vapour species diagram.
- Generally, six types of oxidation phenomena are identified during high temperature process.
- The kinetics of corrosion processes occurring in aqueous medium are chemically monitored

5.8 Keywords

Ellingham diagrams is visualized by the relative stability of metals and their oxidized products .

Vapour species which are formed in the corrosive environment have a strong influence over rate of high temperature corrosion process and the rate is governed by the nature of volatile corrosion products.

The parabolic rate law assumes that the diffusion of metal cations or oxygen anions is the rate controlling step and is derived from Fick's first law of diffusion.

Intergranular corrosion process the grain interiors remains unattached or sometimes slightly corroded.

5.9 Self Assessment and Exercise

1 Explain about the oxide microstructures and rate laws.
2 Explain about galvanic corrosion
3 Explain about the oxide microstructures and rate laws.
4 Explain about Ellingham diagrams
5 Give an account on activation polarization process.

5.10 FURTHER READING

1. D.Jones - Principles and prevention of corrosion, Macmillan Publications New York, (1992).
2. J.J. Meketta - Cathodic Protection Theory and practice, Marcel Dekker Publication, New York, (1993).
3. S.N. Banerjee - An introduction to corrosion and corrosion inhibition, Oxonian Press Ltd., New Delhi.
4. L.L. Shrier - Corrosion Vol I & II Goege Nouns Ltd., Southampton Street, London.
5. M.G. Fontana & N D Greene - Corrosion Science and Engineering. McGraw Hill Book Co., New York.

UNIT -6: Corrosion Control Methods

Structure

6.0 Introduction

Corrosion causes damages to machineries, tools, equipments, fabricated structures and similar other metal parts. It creates additional expenses in addition to the regular maintenance cost. Corrosion takes various forms depending on the conditions of the metal being corroded. To overcome the same various protective measures are under taken which are to be discussed in the succeeding sections.

6.1 Objectives

After going through this unit you are able to

- understand the need for corrosion control
- classify the corrosion control methods
- identify the various corrosion control methods

6.2 General Classification of Corrosion Control Methods

Corrosion protection processes are classified as active control, passive control, permanent control and temporary control. Corrosion takes various forms depending on the conditions of the metal being

NOTE

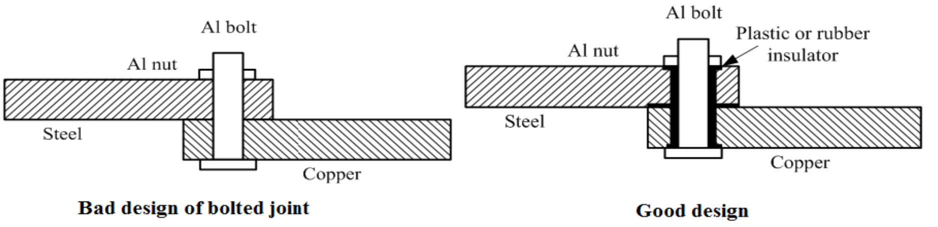
corroded. The following methods are used to protect metals against corrosion process

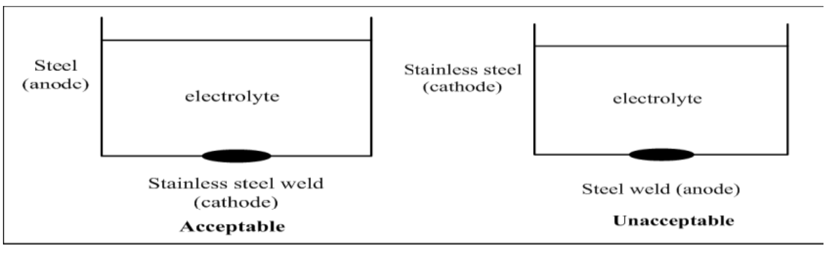
- Designing aspects in corrosion control – Passive Control Process
- Corrosion Inhibitors – Active control Process
- Electrochemical methods of protection– Active Control Process
- Selection of the material – Permanent Control Process
- Surface coating – Passive Control Process

6.3 Designing Aspects in Corrosion Control

The design of the material should be done in such a way that the corrosion even if it occurs after protection must not result in intense form. The designing principles are

- Avoid the contact of dissimilar metals in the presence of a corroding solution.
- When two dissimilar metals are to be contacted, then the anodic material should have as large area as possible whereas the cathodic metal should have smaller area as possible. The two dissimilar metals chosen for contact should be as close as possible to each other in the electrochemical series.Whenever the direct joining of dissimilar metals is unavoidable an insulating fitting may be applied in-between them.





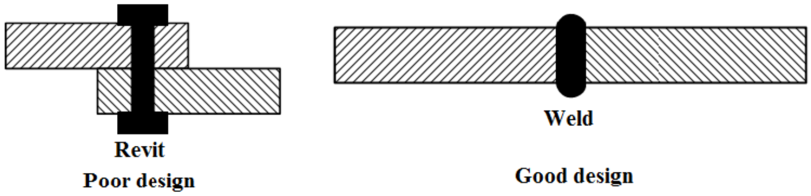


Figure 6.1 Good and bad designs

- The anodic metal should not be coated when in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.
- Prevent the occurrence of inhomogeneities, both in the metal and in the corrosive environment. Proper design should avoid the presence of crevices between adjacent parts of the structure because crevices permit concentration corrosion. Bolts and rivets are therefore undesirable in machineries and these should preferably be replaced by a butt-weld. When it is impractical to avoid crevices in a given design then their harmful effects should be minimized.
- It is desirable that the design allows for adequate cleaning and flushing of the critical parts i.e., susceptible to dirt, deposition, etc.) of the equipment. Sharp corners and recesses should be avoided, because they favour the formation of stagnant areas and accumulation of solids, etc. (see below Fig.).

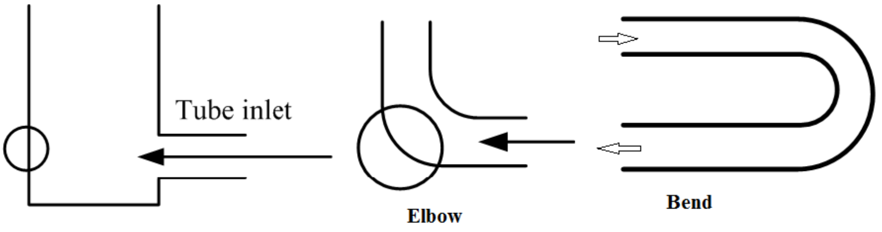


Figure 6.2 Desirable design for adequate cleaning

- Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas .
- Uniform flow of a corrosion liquid is desirable, since both stagnant areas and highly turbulent flow and high velocities can cause accelerated corrosion. So, highly impingement conditions of flowing liquid should be avoided as much as practically possible.

NOTE

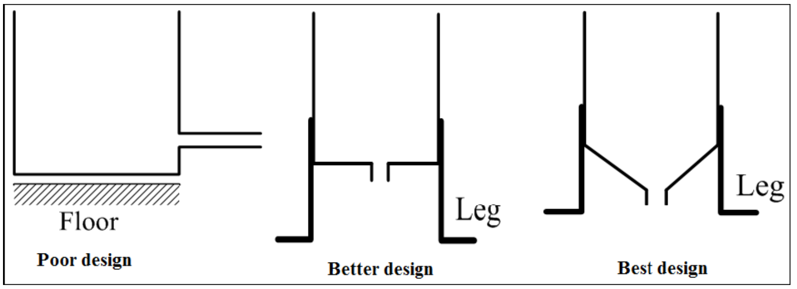


Figure 6.3 Flow desirable designs

6.4 Corrosion inhibitors

A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment effectively decreases the corrosion rate of a metal. Corrosion inhibitors work by one or more of the following ways.

• They adsorb on metal surfaces to form protective films.
• They combine with corrosion product films to protect metal surfaces.
• They form precipitates, which visibly coat and protect metal surfaces.

Classification of inhibitors

Inhibitors can be divided into two main categories as inorganic and organic inhibitors. Inorganic inhibitors are used mainly in boilers, cooling towers, and fractionation units. Organic inhibitors are used mainly in oil field systems.

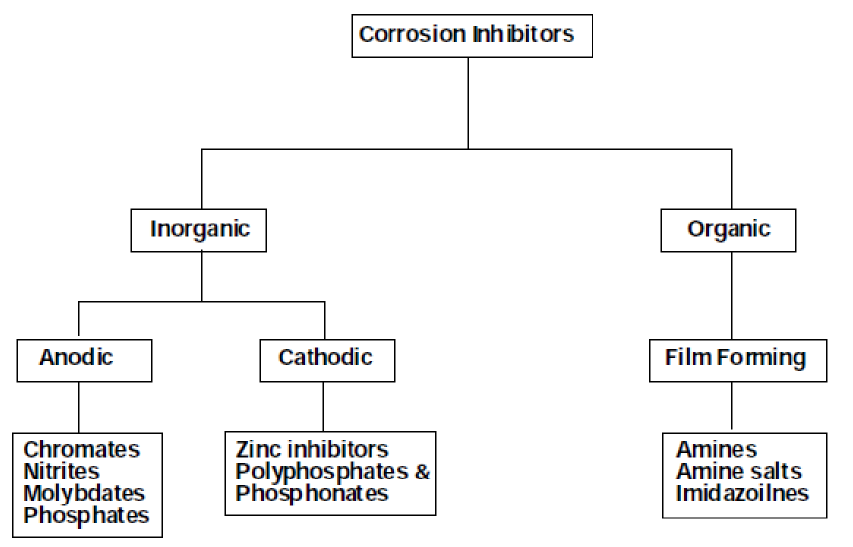


Figure 6.4 Types of inhibitors

As shown in the Figure6.4, inorganic inhibitors are further divided into anodic and cathodic classifications. These classifications

describe the part of the electrochemical process that is interrupted by the inhibitor. Organic film-forming inhibitors interrupt both the anodic and cathodic processes.

Classification of corrosion inhibitors

Inorganic inhibitors

Cathodic inhibitors

Cathodic inhibitors are chemical compounds which inhibit the cathodic reaction of the corrosion cell. Compounds such as $ZnSO_4$, $MgSO_4$ and $Ca(HCO_3)_2$ inhibit the cathodic reaction by forming insoluble films like $Zn(OH)_2$, $Mg(OH)_2$ and $CaCO_3$ film with the cathodically formed ions in neutral solutions. Secondly, oxygen scavengers such as sodium sulphite or hydrazine which react with dissolved oxygen and remove it from the neutral or alkaline corrosive environment

$$2\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N2 + 2H_2O$$

Compounds such as arsenic (As), mercury (Hg), antimony (Sb) salts which are added to acidic corrosive environments to slowdown the cathodic H_2 evolution reaction. These compounds prevent the hydrogen atoms from forming hydrogen gas and are called cathodic poisons.

Anodic inhibitors:

Chemical compounds which inhibit the anodic reaction of the formed corrosive cells are called as anodic inhibitors. Compounds such as Na_2SiO_3, Na_2CO_3 and Na_3PO_4, reacts with Fe^{2+} ions of anode to form an insoluble film of iron silicate or iron carbonate or iron phosphate respectively and retards corrosion cells process. Oxidizing agents such as chromate ions ($Na_2Cr_2O_7$) or nitrite ions ($NaNO_2$) react with Fe^{2+} to form a passive oxide film on the anodic sites of the corrosion cells. They are adsorbed on the metal surface forming a protective film or barrier thereby reducing the corrosion rate. Although this type of control is effective yet it may be dangerous since sever local attack can occur if certain areas are left unprotected by depletion of the inhibitor. Chromate inhibitors contain sodium chromate, Na_2CrO_4, or sodium dichromate, $Na_2Cr_2O_7$. Chromate, or dichromate, ions accept electrons that are lost in ferrous iron oxidation reactions. This reduction reaction forms chromium (III) oxide. The chromium oxide combines with iron oxide to form a mixed oxide. This combination of iron oxide and chromium oxide makes chromium inhibitors effective. Normally, iron oxide deposits are loosely attached to metal surfaces. However, the combination of iron oxide and chromium oxide forms a deposit that tightly attaches to the metal surface. Application of chromate inhibitors are environmental restricted due to its toxicity. More recently zinc phosphate is being used instead of chromates.

Nitrite inhibitors are used to replace the more toxic chromates. Sodium nitrite ($NaNO_2$) is used in closed recirculating cooling water

NOTE

systems with a pH between 7 and 9. Nitrites perform similarly to chromates. They form a protective iron oxide film that passivates steel surfaces. Nitrites can reduce corrosion rates to less than 2 mpy. They are environmentally acceptable and easy to monitor.

Organic Inhibitors: (Adsorption inhibitors)

These are organic compounds which contain a hetero atoms such as N,O,S or π electron containing compounds adsorb on the metallic surface and isolate it from the corrosive solution.

Organic corrosion inhibitors are complex mixtures of many different molecular compounds. Organic inhibitors typically affect both anodic and cathodic areas of corrosion cells. They lay down an organic film on the entire metal surface. Their effectiveness depends upon the following conditions:

- the electrical potential of the metal
- the chemical structure of the inhibitor molecule
- the size and shape of the inhibitor molecule

An organic corrosion inhibitor molecule consists of a hydrocarbon chain that is attached to a strongly polar functional group. The hydrocarbon chain of the inhibitor molecule is oil soluble. This chain provides a barrier that keeps water away from the metal surface. Polar functional groups are based on nitrogen, sulfur, or oxygen.

Organic inhibitor molecules attach to metal surfaces by chemisorption and physical adsorption. When a metal is in contact with an aqueous solution, most of the metal surface is covered with adsorbed water molecules. If an organic inhibitor is introduced into the system, the unshared electrons in the polar group form a chemisorption bond with the metal surface. The chemisorption bond displaces water molecules and other corrosive agents from the metal surface. The long hydrocarbon chains also play an important part in the inhibition process. The hydrocarbon chains are oil soluble and attract crude oil molecules in the process stream. This oily layer acts as a barrier against corrosive fluids. The oily layer also increases the film life of the inhibitor. In addition to the chemisorption bond, organic inhibitors also physically adsorb to the metal surface. Physical adsorption is weaker than chemisorption. Physical adsorption does not involve a sharing of electrons with the metal surface.

6.5 Electrochemical Methods of Protection Such as Anodic and Cathodic Protection

The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion does not occur. Cathodic protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode. This is achieved by

applying a current to the structure to be protected from some outside source. When enough current is applied such that the the whole structure will have no potential difference and restricts corrosion. Cathodic protection is commonly used on many types of structures such as pipelines, underground storage tanks and ship hulls.

Types of cathodic protection systems

There are two main types of cathodic protection systems:

a) Sacrificial anodic protection
b) Impressed current cathodic protection

a) Sacrificial anodic protection

A galvanic cathodic protection system makes use of the corrosive potentials for different metals. Without cathodic protection, one area of the structure exists at a more negative potential than another, and corrosion results. If, however an active metal that is, with more negative potential is placed adjacent to the structure with metallic connection, then the metal will become anode to the entire structure. The metal corrodes sacrificially to protect the structure as shown in Figure 6.5. Thus the galvanic cathode protection system is called a sacrificial anode cathodic protection system because the anode corrodes sacrificially to protect the structure. Galvanic anodes are usually made of either magnesium or zinc because of these metals higher potential compared to steel structures.

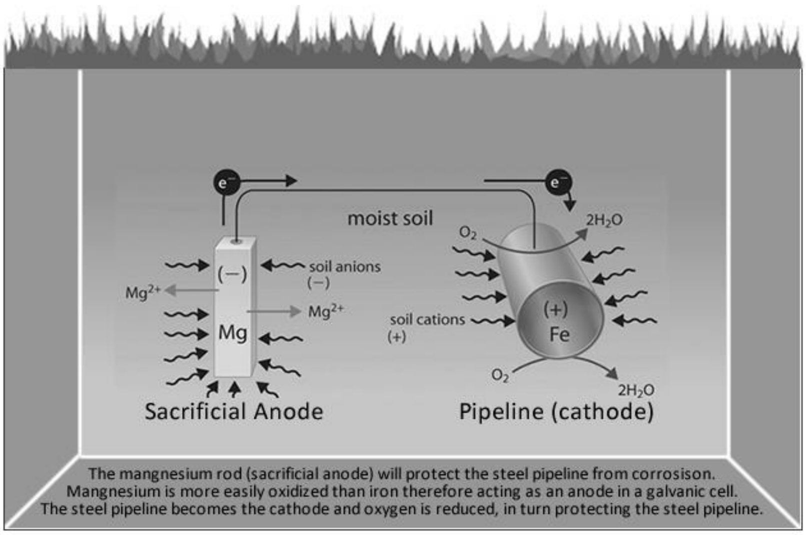


Figure 6.5 Sacrificial anodic protection

b) Impressed current cathodic protection

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal

from anode to cathode. Usually, the impressed current is derived from a direct current source like battery or rectifier on a.c. line with an insoluble anode like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually, a sufficient D.C. current is applied to an insoluble anode, buried in the soil or immersed in the corroding medium), and connected to the metallic structure to be protected. The anode is, usually, in a backfill composed of coke breeze or gypsum so as to increase the electrical contact with the surrounding soil. This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. This kind of protection technique is, particularly, useful for large structures for long-term operations.

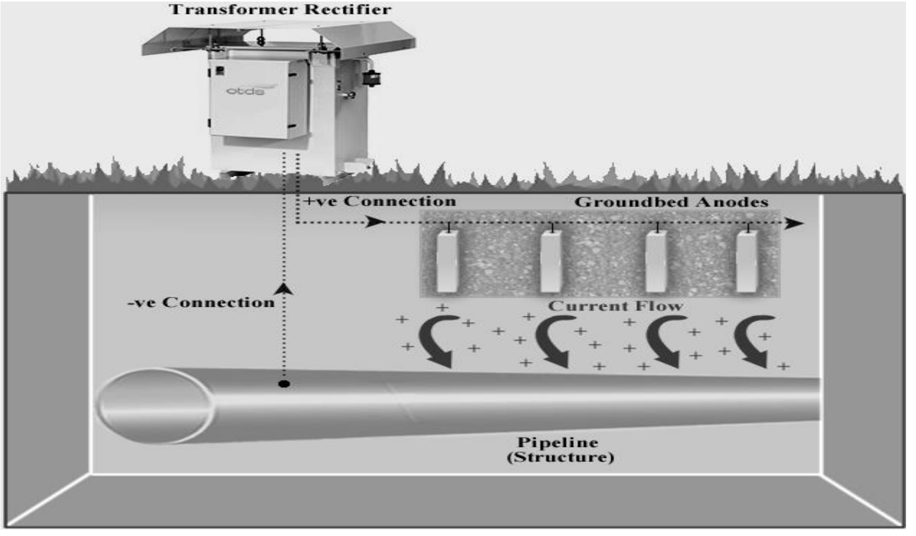


Figure 6.6 Impressed current cathodic protection

6.6 Selection of the Material

The right material of construction should have the properties such as high mechanical strength, high corrosion resistance and cost. The material selection is carried out through the following steps

1. Preliminary selection based on experience, availability and safety aspects

2. Laboratory testing and evaluation of suitable materials

3. Effect of possible corrosive environments and their influence on material of choice

4. Economic comparison such as maintenance,cost, probable life, cost of product

degradation, and liability to special hazards

5. Final selection

Some of the points illustrating the present study are discussed below

6.6.1 Usage of pure metal and alloys

Impurities in a metal cause heterogeneity which decreases corrosion-resistance of the metal. The corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces when exposed to environment. However, in many cases, it is not practical to produce a metal of high chemical purity because of cost and very pure metal often possesses the disadvantages of inadequate mechanical properties like softness and low strength. Corrosion-resistance of most metals is best increased by alloying them with suitable elements. Chromium is the best suitable alloying metal for iron or steel. Its film is self-healing. Steel containing up to 13% Cr are used in cutlery, surgical instruments, springs, etc. Ferrite stainless steels containing 13 to 25% Cr are used in turbine brackets, heat-resisting parts, etc.

6.7 Surface coatings

Protecting the surface of a metal by the application of coating is a common procedure for corrosion control. A coated-surface protects the underlying metal from the corroding environment. The coat applied must be chemically inert to the environment under particular conditions of temperature and pressure. Coatings must prevent the penetration of the environment into the material. There are two types of surface coating as depicted in the following Figure 6.7.

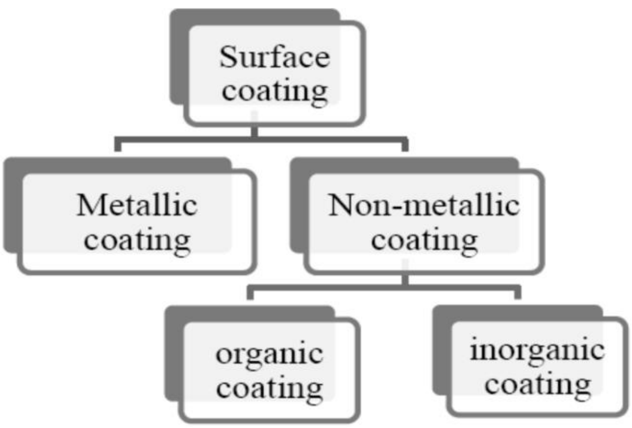


Figure 6.7 Classification of protective coatings

6.7.1 Metallic Coating

The structure (base metal) is coated with a layer of other metal (coat metal) which may be more noble than the or less noble than the structure to be protected. For e.g., protection of steel structures using copper (more noble) or zinc (less noble) coatings. The coating should be able to resist direct attack of the environment. The coating should be nonporous and continuous (no cracks) to a void acceleration of corrosion especially in case of a more noble metal. The coating should be hard. Coating the structure with a more noble metal should be carefully monitored because the development of pores or cracks on the coat would lead to galvanic corrosion. The development of cracks on coat surface does not affect the base metal because galvanic corrosion will concentrate on coat metal. In practice metallic coating is carried out by the following ways

- Electroplating of base metal
- Hot dipping of the base metal in molten coat metal
- Spraying of the molten coat metal on the base metal

6.7.1.1 Electroplating

Electroplating is the method of coating one metal on metal using electricity. It is most commonly used for decorative purposes, appearance and protection. Electroplated items include chrome bumpers, jewelry, electronics, circuit boards and airplane parts.

During plating, the base metal should be cleaned with solutions such as alkaline cleaners, solvent degreasers or acidic pickling mixtures are used to remove dirt, greases, oxidation and contaminants from the piece. The base metal to be plated is connected to the cathode while the coat metal serves as anode in presence of an electrolytic solution. By varying cell current and voltage effective coatings are obtained. Then the coated metal immersed in the plating solution, rinsed and then buffed or polished. The plating time depends on the required thickness and obeys the Faraday's law. The quality of coating depends on average thickness of coating, porosity uniform thickness and adherence.

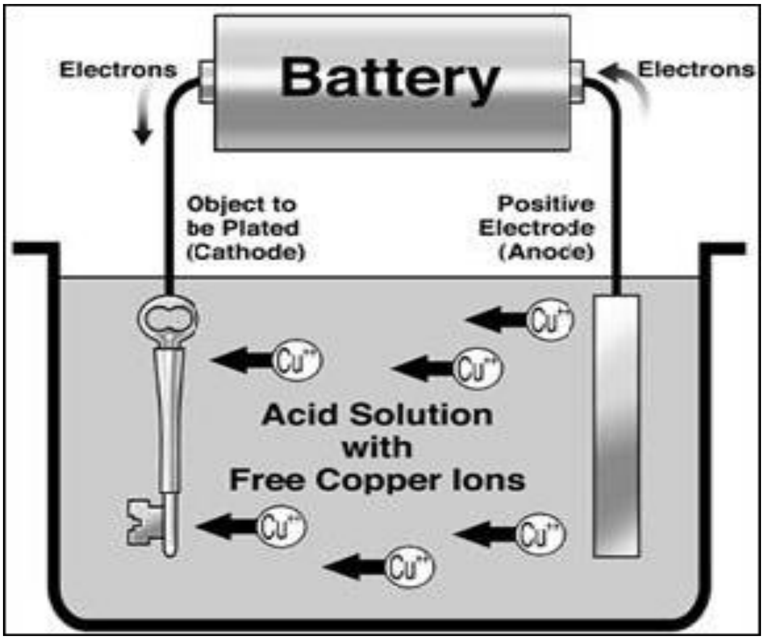


Figure 6.8 Electroplating of copper on article to be protected

6.7.1.2 Hot Dipping

It is a hot coating process whereby the base metal is immersed in molten coat metal usually at a elevated temperature as governed by metallurgical laws. As a result of this process the coating consists of a series of alloy layers which are inter-metallic in nature are formed and a top pure coat layer. The adhesion of the coating to the base metal is superior and avoids corrosion. A hot dipped galvanized coating will provide greater corrosion protection to steel when compared to that of an electroplated product.

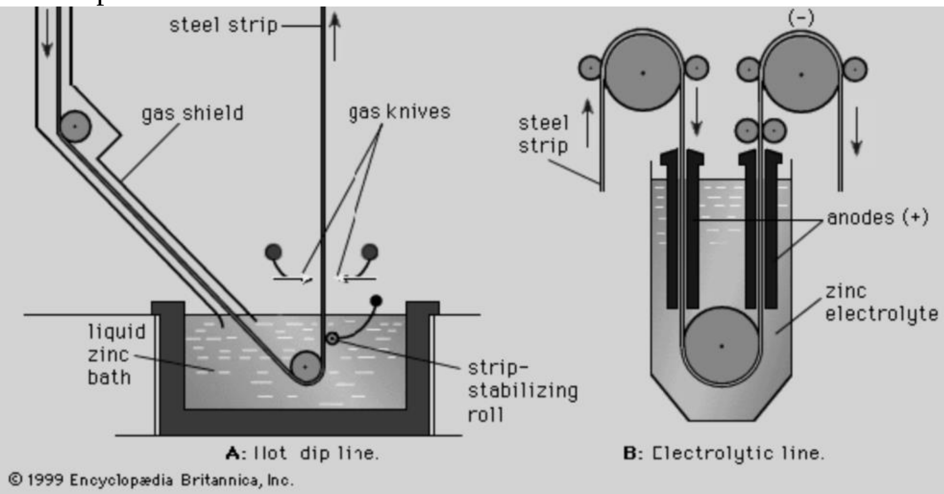


Figure 6.9 Hot dipping of steel (base metal) in molten zinc (coat metal)

6.7.1.3 Spraying of the molten metal on the base metal

NOTE

Thermal spraying is a process by which a metal wire or powder is melted and sprayed onto a surface to form a coating. A thermal spray gun is used to apply the coatings. The thermal spray gun heats the metallic wire or powder to a molten state and compressed air or other gas propels it onto the surface to form a coating. The compressed gas also aids in division and atomization of the molten coating. The two metals most commonly applied by thermal spray are zinc and aluminum. These metals and their alloys provide excellent protection in a variety of marine and industrial corrosive environments. Similar type of protection is also offered by non-metallic coatings.

2. Using pure metal: Impurities in a metal cause heterogeneity, which decreases corrosion-resistance of the metal. Thus, the corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces, when exposed to environment. However, corrosion-resistance of a purified metal depends on the nature of corrosive environment. For example, the corrosion resistance of AI depends on its oxide film formation, which is highly protective only on the high purity metal. However, nothing is gained by purifying Al, if it is to be used in alkaline environment, in which both the oxide film and the Al are destroyed.

In many cases, it is not practical to produce a metal of high chemical purity, because : (1) of cost consideration in some cases, and (2) very pure metal often possesses the disadvantages of inadequate mechanical properties like softness and low strength. Thus, the greater thickness of pure metal is required for a proper strength. Generally, purification of metals is of use only under conditions in which corrosion by a purely electrochemical mechanism and not by direct chemical attach.

3. Using metal alloys : Noble, but precious metals such as platinum and gold are corrosion-resistant. Corrosion-resistance of most metals is best increased by alloying them with suitable elements, but for maximum corrosion-resistance, alloy should be completely homogeneous. Chromium is the best suitable alloying metal for iron or steel. Its film is self-healing. Thus, steel containing up to 13% Cr are used in cutlery, surgical instruments, springs, etc. Iron alloys containing 13 to 25% Cr (called "ferrite stainless steels" are used in turbine brackets, heat-resisting parts, etc.

4. Cathodic protection: The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.

There are two types of cathodic protections:

(i) **Sacrificial anodic protection method:** In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so-employed is called "sacrificial anode". The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, ship-hulls, water-tanks, piers, etc.

(ii) **Impressed current cathodic protection:** In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum). Usually, a sufficient d.c. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected. The anode is, usually, in a backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This ype of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. This kind of protection technique is, particularly, useful for large structures for long-term operations.

5. Modifying the environment: The corrosive nature of the environment can be reduced either : (i) by the removal of harmful constituents, or (ii) by the addition of specific substances, which neutralize the effect of corrosive constituents of the environment.

(a)**Deaeration.** In oxygen concentration type of corrosion, exclusion of oxygen from aqueous environment reduces metal corrosion. Expulsion of dissolved oxygen is done by adjustment of temperature, together with "mechanical agitation. The method also reduces the CO_2-content of water, thereby decreasing the corrosion rate of steel pipelines carrying steam condensates from boilers.

(b) **Deactivation** involves the addition of chemicals, capable of combining rapidly with the oxygen in aqueous solution. For example, sodium sulphite (Na_2SO_3).

$$2\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

Hydrazine hydrate (NH_2. NH_2. H_2O) is advantageous over the sodium sulphite, because the reaction products are N_2 (g) and water.

$$N_2H_4 + O_2 \rightarrow N2 + 2H_2O$$

(c) **Dehumidification** reduces the moisture content of air to such an extent that the amount of water condensed on metal is too small to cause corrosion. Alumina or silica gels, which adsorbs moisture preferentially on their surfaces, are used only in closed areas like air-conditioning shop.

d) **Alkaline neutralization** is prevention of corrosion by neutralizing the acidic character of corrosive environment (due to the presence of H_2S, HCl, CO_2, SO_2, etc.). Such alkaline neutralizers (like NH_3, NaOH, lime, naphthenic soaps, etc.) are, generally, injected either in vapour or liquid form to the corroding system or to its parts. This method has been widely used in controlling the corrosion of refinery equipments.

6. **Use of inhibitors :** A corrosion inhibitor is "a substance which when added in small quantities to the aqueous corrosive environment, effectively decreases the corrosion of a metal". Inhibitors are:

(i) Anodic inhibitors (such as chromates, phosphates, tungstate's or other ions of transition elements with a high oxygen content) are those that stifle the corrosion reaction, occurring at the anode, by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate. Although this type of control is effective, yet it may be dangerous, since sever local attack can occur, if certain areas are left unprotected by depletion of the inhibitor.

(ii) Cathodic inhibitors: (a) In acidic solutions, the main cathodic reaction is evolution of hygrogen.

$$2H^+(aq) + 2e^- \rightarrow H2\ (g)$$

Consequently, corrosion may be reduced either by slowing down the diffusion of hydrated H^+ ions to the cathode, and /or by increasing the overvoltage of hydrogen evolution. The diffusion of H^+ ions is considerably decreased by organic inhibitors (like amines, mercaptans, hetrocyclic nitrogen compounds, substituted ureas and thio-ureas, heavy metal soaps), which are capable of being adsorbed at the metal surfaces. Antimony and arsenic oxides (or salt like sodium meta-arsenite) are used as inhibitors, because they deposit adherent film of metallic arsenic or antimony at the cathodic areas, thereby increasing considerably the hydrogen overvoltage.

(b) In natural solutions, the cathodic reaction is

$$H_2O\ (e) + \frac{1}{2}O_2 + 2e^- == 2OH^-\ \ (aq)$$

The corrosion can, therefore, be controlled either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic areas. The former is, usually, attained by adding reducing agents (like Na_2SO_3) or by deaeration. The inhibitors like Mg, Zn or Ni salts to the environments are used in the latter case. These react with hydroxyl ions (at the cathode) forming corresponding insoluble hydroxides, which are deposited on the cathode forming more or less impermeable self-barriers.

7. **Application of protective coatings :** Protecting the surface of an object by the application of coating is probably the oldest of the common procedures for corrosion prevention. A coated-surface isolates the underlying metal from the corroding environment. The only limitations of this method is the service behaviour of the protective coatings : (i)The coating applied must be chemically inert to the environment under particular conditions of temperature and pressure. (ii) Moreover, coatings must prevent the penetration of the environment to the material, which they protect.

8. **Potentiostatic anodic protection:** It may be pointed that metals like Ti and ferrous alloys like stainless steel cannot afford cathodic protection, since these readily get passivated. The basic principle of anodic protection is "the growth of protective oxide surface film by the application of anodic current on the metal alloy appliance in a suitable, oxidising atmosphere". The required potential for protecting the metal/alloy can be obtained from its "potential-current curve". At an appropriate predetermined applied potential values, the changes in the observed potential versus changes in the current are plotted (see Fig. 24). Initial curve AB indicates increase in current, thereby indicating the corrosion (or dissolution) of the metal/alloy at the anode. When the current assumes a critical value (I_{crit}), onset of development of protective surface oxide film is indicated. The potential (E_{crit}) at critical value of current, is known as critical passivation potential for the metal/alloy. Above E_{crit} (i.e., along curve BC), the current flowing drops to a very small value, called the passivation current (I_p), which may be defined as "the minimum protective current density needed to maintain passivation in the metal/alloy". Corresponding value of potential is called passivation potential (E_p). At this stage (at C in the curve), minimum corrosion of the metal/alloy will take place, because the latter is already in a fully passive state. Thus, only a very small current (I_p) if maintained is capable of

keeping the metal/alloy in passive state, thereby reducing considerably the corrosion rate.

The metallic alloy specimen (to be protected) is made anode in a suitable oxidising medium (atmosphere).The potential is increased slowly to E_p value, to allow initial corrosion to take place. Then, the value of potential is increased slightly to E_f (fade potential) so that current is always maintained at a very small value (I_p). Thus, by maintaining the values of both E_f and I_p, the specimen always remain in passivated state.

Limitations: (i) During anodic protection method, the corrosion does take place, but at a very slow rate. In other words, corrosion rate is not zero.

(ii) This method can be applied only to those metals/alloys which passivate.

Applications: Stainless steel containers used for transporting corrosive chemicals (e.g., concentrated acids) are protected from corrosion by passivating them by maintaining them at proper E_f and I_p.

6.8 Check Your Progress Questions

1. Give the general classification of corrosion control methods.
2. How the corrosion inhibitors will function during inhibition.
3. Name the factors which influence the organic corrosion inhibitors.
4. Define cathodic protection.
5. What are the properties to be considered while selecting a material for fabrication?

6.9 Answer to Check Your Progress Questions

1.General classification of corrosion control methods are:

- Designing aspects in corrosion control – Passive Control Process
- Corrosion Inhibitors – Active control Process
- Electrochemical methods of protection– Active Control Process
- Selection of the material – Permanent Control Process
- Surface coating – Passive Control Process

2. Corrosion inhibitors work by one or more of the following ways.

They adsorb on metal surfaces to form protective films.

They combine with corrosion product films to protect metal surfaces.

They form precipitates, which visibly coat and protect metal surfaces.

3. The effectiveness depends upon the following conditions:

- the electrical potential of the metal

- the chemical structure of the inhibitor molecule
- the size and shape of the inhibitor molecule

An organic corrosion inhibitor molecule consists of a hydrocarbon chain that is attached to a strongly polar functional group.
4. Cathodic protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode.
5. The right material of construction should have the properties such as high mechanical strength, high corrosion resistance and cost

6.10 SUMMARY

Corrosion protection processes are classified as active control, passive control, permanent control and temporary control. Corrosion takes various forms depending on the conditions of the metal being corroded. The following methods are used to protect metals against corrosion process.

The design of the material should be done in such a way that the corrosion even if it occurs after protection must not result in intense form.

Organic film-forming inhibitors interrupt both the anodic and cathodic processes.

The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion does not occur. Cathodic protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode.

The corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces when exposed to environment.

6.11 Keywords

A **corrosion inhibitor** is a substance which when added in small quantities to the aqueous corrosive environment effectively decreases the corrosion rate of a metal.

Cathodic inhibitors: are chemical compounds which inhibit the cathodic reaction of the corrosion cell.

Anodic inhibitors: Chemical compounds which inhibit the anodic reaction of the formed corrosive cells.

Electroplating is the method of coating one metal on metal using electricity.

6.12 Self Assessment Questions And Exercises

1. Write a note about designing aspects of Corrosion Control.
2. What are corrosion inhibitors?
3. Write a note on cathodic control process.
4. Describe the usage of pure metal and alloys in corrosion control.

Unit -6: Corrosion Control Methods

NOTE

6.13 Further Reading

1. L.L. Shrier - Corrosion Vol I & II Goege Nouns Ltd., Southampton Street, London.
2. M.G. Fontana & N D Greene - Corrosion Science and Engineering. McGraw Hill Book Co., New York.
3. D. Jones - Principles and prevention of corrosion Macmillan Publications New York, (1992).
4. J.J. Meketta - Cathodic Protection Theory and practice, Marcel Dekker Publication, New York, (1993).
5. S.N. Banerjee - An introduction to corrosion and corrosion inhibition, Oxonian Press Ltd., New Delhi.

Block -3: Electrochemistry - II

Unit-7: Electroplating

Structure

7.0 Introduction

Electroplating is the application of coatings to metals or other conductive surfaces by electrochemical processes. Electroplating is done for decorative and corrosion control measures. The metal finishing science has its base from chemistry and includes other areas such as physics, chemical and electrical engineering, metallurgy. All these sciences have elements of art which can be learned and applied to control a nature driven process. There are numerous applications of electroplating as stated below. Copper is an excellent conductor of electricity and is therefore basic to such items as printed circuits and communications equipment. It does, however, quickly form tarnish films that interfere with joining operations such as soldering and that also render contact resistances unacceptably high in relays and switches. To make soldering easier, coatings of tin or tin-lead alloys are often applied to copper, and for better contacts overplates of gold are frequently required. Other surface properties may call for modification; if light reflection is important, a silver or rhodium plate may be necessary. In wave guides for radar, high electrical conductivity is the most important criterion, and silver is the preferred coating. Good bearing properties may require coatings of tin, lead or indium. If a hard surface is required, chromium or nickel usually will serve. These few examples illustrate

NOTE

another use of metal finishing; to modify the surface properties, either physical or chemical, to render them suitable for the intended use.

7.1 Objectives

After going through this unit you are able to

- Acquire knowledge about the process of electroplating
- Gain familiarity about throwing power experiment
- Understand the various methods of surface preparation

7.2 Principles of electroplating

Electroplating (Electrodeposition) is the process by which thin layers of selected metal are coated on the surface of base metal by passing direct current through an electrolytic solution. The process of electroplating is done in an electrolytic cell and the plated material possesses

- Corrosion resistance
- Decorative appearance
- Improved surface properties
- Good mechanical strength

The common examples are the plating of base metal with metals such as copper, silver & chromium and the plated materials finds wider application in automobile, airplanes, electronics, jewelery, and toy industries.

7.3 Metal deposition from solutions of simple salts

Figure 7.1 illustrates a typical electroplating setup for plating silver on a spoon from a solution of silver nitrate. The article to be coated (base metal - spoon) is made as cathode by connecting it to the negative terminal of the battery and the coat metal is made as anode by connecting it to the positive terminal of the battery. The Ag^+ ions present in the solution undergoes reduction at the cathode forming a smooth surface of metallic silver on spoon. Concurrently, the same number of nitrate ions NO_3^- reaches the silver anode thereby forming a new quantity of silver nitrate and maintains solution concentration.

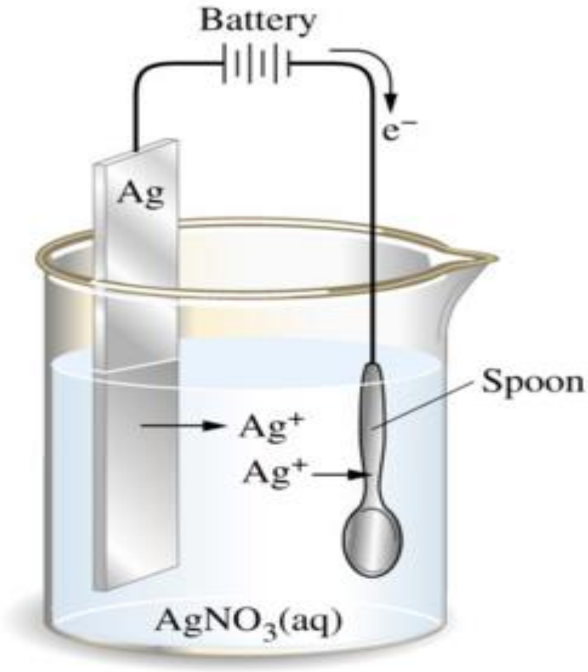


Fig. 7.1: Electroplating of silver on spoon

At the cathode

$Ag^+ + e^- \longrightarrow Ag$

At the anode

$Ag \longrightarrow Ag^+ + e^-$

7.4 Metal deposition from solutions of complex salts

On complexing the metal-ion with a complexing agent, fine-grained and more adherent deposits are obtained. Complexing agents are employed:

(i) when the cathode metal and plating metal ions as such are known to react, eg., during plating of Cu on Fe, the plating ion Cu^{2+} is complexed with CN^- ions so as to avoid the reaction:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

(ii) to make the potential of the plating metal-ions more negative in order to carry out plating at a lower potential.

(iii) to avoid the passivation of anodes so that these can dissolve more easily, thereby leading to enhanced current efficiency.

(iv) to enhance the throwing power of the plating bath solution. This is frequently accomplished by employing complexing agents like cyanide, hydroxide, etc. Smooth and adherent deposits of Cu, Ag. Au, Cd, Zn, etc. are obtained in the presence of CN^- ions.

NOTE

7.5 Measurement of Current Density

Current density is the ratio of quantity of electric current to the surface area of exposture. During plating the thickness, smoothness and other desirable properties for finishing are achieved using current density.

$$\text{Current density} = \frac{\text{Current in amperes}}{\text{Exposed Area in m}^2}$$

7.6 Determination of throwing power

It is determined by using Haring-Blum cell which consists a cell containing the plating bath solution under test. It has an anode at the centre and two cathodes, whose surfaces away from the anode are insulated. These electrodes are placed at a respective distance of d_1 and d_2 ($d_1 > d_2$) from the anode. Electroplating is carried out for an appropriate time and weights of metal (w_1 and w_2 respectively) deposited on the two electrodes are determined. then throwing power of the plating bath solution

Throwing power = $\frac{(x-y)X100}{(x+y-2)}$ per cent, where

$x = d1/d2$ and $y = w_2/w_1$.

(i) When $w_1 = w_2$ (i.e., same amount of metal is deposited irrespective of the placement of the eléctrode), then throwing power is considered very good (100%).

(ii) When the value of calculated throwing power is- 100%, then it is considered as very poor.

7.7 Surface Preparation for Electroplating

(i)Solvent cleaning is used to remove oils, greases, buffing compounds, and fatty substances. This involves in cleaning the surfaces by the application of organic solvents like naphtha, chlorinated hydrocarbons (like carbon tetrachloride), toluene, xylene or acetone. This is followed by cleaning with steam and hot water, containing wetting agents and alkalis. This treatment provides a metal surface, readily wetted by aqueous solution, which is particularly required for electroplating.

(ii) Alkali cleaning is particularly well-adapted for the removal of old paint coating from metal surfaces. Alkali cleaning agents are trisodium phosphate along with soaps and wetting agents like caustic soda. An alkali treatment is always to be followed by a very thorough rinsing with water and then immersion in a slightly acidic solution of 0.1% chromic acid (or sodium or potassium chromate) to remove the last traces of alkalis. Alkali cleaning method con be made more effective by the application of an electric current, and making the "metal cathodic" in alkaline medium. The copious evolution of hydrogen at the cathode metal results in strong agitation, which helps to disoldge the oily substances.

(iii) Mechanical cleaning removes loose rust and other impurities from the surface. This is, generally, done by hand cleaning with a bristle brush plus some abrasive (like sand) and detergent (like soap). Impact tools like dull chisels, knife scrapers, wire brushes, grinding wheels and cutters are also used for removing strongly adhering scales, etc. The remaining dust and loose particles of dirt are then removed by solvent cleaning, followed by steam or hot water treatment.

(iv) Flame cleaning is accomplished by heating the metal surface with a hot flame to remove moisture and loosely adhering scales. This is followed by wire brushing.

(v) Sand-blasting is used for removing oxide scales, particularly when a slightly roughened surface is desired. Paint coatings on sand-blasted surface are, particularly, more durable than those on metal surfaces cleaned by other methods. Sand-blasting is especially suitable for large steel surfaces and should always be used, whenever maximum protection from the coating is required. However, the process requires expensive equipment and the sand-blasting operation is dangerous to health of workers, because of the possibility of disease, 'silicosis', unless special protective measures are taken. The process consists in introducing the sand (an abrasive) into an air stream, under pressure of 25 to 100 atmospheres. The blast is impacted on the metal surface to be cleaned. The sand-blast impact removes any scale present and also causes a certain degree of hardening of the cleaned metal surface.

(vi) Pickling and etching Acid pickling is more convenient method of scale removal in many cases than mechanical cleaning and sand-blasting. It is, usually, accomplished by immersing the metal (except Aluminium) in an acid-pickling solution. Aluminium is picked in alkaline solution.

Acid-pickling of steel is accomplished by dipping in warm dil. H_2SO_4 or in cold HCl solution to which some "inhibitor" has been added.

NOTE

For cleaning of articles made of copper, brass or nickel, the pickling bath consists of dilute HNO_3 or a mixture of dil. HNO_3 and dil. H_2SO_4. If the cleaning operation is carried out in an efficient manner, it provides a clean, smooth surface for electrodeposition. Moreover, the deposit obtained is adherent, tough, smooth, and bright in appearance.

7.8 Measurement of Current efficiency

A known metal (A) is deposited with or without coating on the another known metal (B) plate substrates from which the mass of A deposited is calculated and labeled as M1. The theoretical mass of A is calculated from the Faraday's law of electrolysis. Let the theoretical amount deposited by spending 1 columb of electricity be M. From M_1 and M the current efficiency was calculated using the following equation.

$$\text{Current efficiency (\%)} = \frac{M_1 x 100}{M}$$

7.9 Electroplating of Nickel and Copper

The following procudures discusses the electroplating procedures of nickel and copper.

7.9.1 Electroplating of nickel

	Sulphate bath	Sulphamate bath
Plating bath composition (per L)	$NiSO_4$ + $NiCl_2$ + boric acid. Rest water.	Ni sulphamate + $NiCl_2$ + boric acid. Rest water.
pH of bath	4.5	4.2
Additives	Coumarin, saccharin, benzene| sulphonamide	Naphtheline 1,3,6-trisulphonic acid
Temperature (^oC)	40-60	50-60
Current density (mA cm^{-2})	20-50	40-400
Anode	Ni pallets or pieces in titanium mesh basket.	Ni pallets or pieces in titanium mesh basket.
Current efficiency (%)	95	97
Throwing power	Medium	Good
Applications	Undercoat for Cr plating.	Decorative purposes and mirror finish at high current

		density (400 mA cm^{-2})

Table 7.1 Electroplating of Nickel

NOTES

7.9.2 Electroplating of Copper

	Sulphate bath	Cyanide bath
Plating bath composition (per L)	$CuSO_4$ + H_2SO_4. Rest water.	CuCN+KCN + K_2CO_3. Rest water
Additives	Gelatin or dextrin, sulphur - containing brightener, sulphonic acid.	Sodium thiosulphate ($Na_2S_2O_3$).
Temperature (^oC)	30	40-75
Currentdensity(mAcm^{-2})	20-50	10-40
Anode	P contained rolled Cu	Oxygen-free high conducting Cu
Current efficiency (%)	93-95	65-90
Throwing power	medium	Good
Applications	In printed circuit boards (not suitable for iron and its alloys plating).	As an undercoat for Cr plating and printed circuit boards (suitable for iron and its alloys plating).

Table 7.2 Electroplating of copper

7.10 Check your progress Questions

1. Explain the principles of Electroplating.
2. What is meant by Current density ? How its measured?
3. Write the use of Sand-blasting.
4. Give the purpose of Sulphamate bath.

7.11 Answers to Check Your Progress Questions

1. Electroplating (Electrodeposition) is the process by which thin layers of selected metal are coated on the surface of base metal by passing direct current through an electrolytic solution.

2. Current density is the ratio of quantity of electric current to the surface area of exposture. During plating the thickness, smoothness and other desirable properties for finishing are achieved using current density.

Current density = Current in amperes

Exposed Area in m^2

3. Sand-blasting is used for removing oxide scales, particularly when a slightly roughened surface is desired.

4. Good decorative purposes and mirror finish at high current density (400 mA cm^{-2}).

7.12 Summary

- Electroplating (Electrodeposition) is the process by which thin layers of selected metal are coated on the surface of base metal by passing direct current through an electrolytic solution.
- The common examples are the plating of base metal with metals such as copper, silver & chromium and the plated materials finds wider application in automobile, airplanes, electronics, jewelery, and toy industries.
- On complexing the metal-ion with a complexing agent, fine-grained and more adherent deposits are obtained. Complexing agents are employed.
- Throwing Power determined by using Haring-Blum cell which consists a cell containing the plating bath solution under test. It has an anode at the centre and two cathodes, whose surfaces away from the anode are insulated. These electrodes are placed at a respective distance of d_1 and d_2 ($d_1 > d_2$) from the anode. Electroplating is carried out for an appropriate time and weights of metal (w_1 and w_2 respectively) deposited on the two electrodes are determined. then throwing power of the plating bath solution

7.13 Keywords

Current density is the ratio of quantity of electric current to the surface area of exposture.

Electroplating (Electrodeposition) is the process by which thin layers of selected metal are coated on the surface of base metal by passing direct current through an electrolytic solution.

Throwing power is determined by using Haring-Blum cell which consists a cell containing the plating bath solution under test.

Acid-pickling of steel is accomplished by dipping in warm dil. H_2SO_4 or in cold HCl solution to which some "inhibitor" has been added.

Flame cleaning is accomplished by heating the metal surface with a hot flame to remove moisture and loosely adhering scales.

Alkali cleaning is particularly well-adapted for the removal of old paint coating from metal surfaces. Alkali cleaning agents are trisodium phosphate along with soaps and wetting agents like caustic soda.

The **current efficiency** was calculated using the following equation.

$$\text{Current efficiency (\%)} = \frac{M_1 \times 100}{M}$$

NOTES

7.14 Self-Assessment Questions and Exercises

1. Explain the process of electroplating
2. Discuss the electroplating procedure of copper plating
3. Give the bath composition maintained during Nickel plating
4. Explain about about throwing power experiment

7.15 Further Readings

1. William H. Safranek The Properties of Electrodeposited Metals and Alloys: A Handbook Amer Electroplaters Soc; Subsequent edition, 1986
2. Metal Finishing Handbook, Elseveit, The Netherlands, 2005.
3. Jack W. Dini, Electrodeposition - The Materials Science of Coating and Substrates Noyes Publications, New York,1993.
4. Frederick A. Lowenheim Electroplating: Fundamentamental of metal finishing Mcgraw Hill, New York, 1978.

Block -3: Electrochemistry - II

Unit-8: Electroforming

Structure

8.0 Introduction

It is a process of forming metals to various shapes which are produced by electrolytic deposition of metal upon a conductive removable mould. The difference between electroplating and electroforming being that in the former case the metal permanently sticks to the cathode whereas in latter case a solid shell is produced around the cathode which can be separated from it. The cathode mould called as mandrel can be made of any shape depending upon the shape required for the part. The finish of products depends upon the surface smoothness of mould. The metal for electroforming the part on the mould is supplied from an electrolytic solution in which a bar of pure metal acts as an anode for the plating current.

8.1 Objectives

After going through this unit you are able to

- Understand about the principle of electroforming process
- Appreciate the various applications of electroforming process.
- Recognize the cladding process of metals

8.2 Principles and applications

Electroforming is an electrodeposition process, similar to electroplating and electrorefining. Therefore, the process requires two electrodes immersed in a conducting electrolyte containing metallic salts and a source of DC power. As current is passed between the two electrodes, metallic ions in solution are converted into atoms on the cathode surface and these build up layer upon layer, micron upon micron to produce a continuous deposit on mandrel. The process is shown schematically in Figure 1.

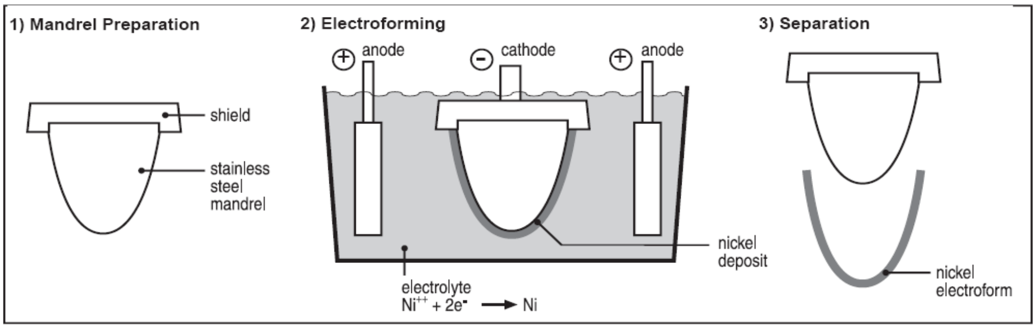


Figure 1 Schematic of an electroforming operation.

Applications of Electroforming

- Electroforming is a process for making metallic articles with good dimensional stability
- A free standing metal object is made by depositing a metal to mandrel
- Reproducible facbrication technique
- complex shaped objects are finishned easily
- Making of moulds
- Decorative coat
- Fabricating medical equipments

8.3 Alloy Plating of brass

An alloy coating may be obtained by a co-deposition of the alloy constituents from the electrolyte containing their ions. Deposited alloys may possess properties and combination of properties, which ate not

achievable in the coatings of pure metals. Electroplating allows to prepare alloys, which cannot be produced by melting. Some metals may be deposited only in form of their alloys. For example electroplating molybdenum (**Mo**), germanium (**Ge**) or tungsten (**W**) is possible only from the electrolytes containing also ions of iron (**Fe**) or nickel (**Ni**).

8.3.1 Role of electrode potentials in electroplating alloys

According to the Faraday's law for electroplating binary alloy composed of two metals **M** and **A**:

$$W_M = I_M*t*\mu_M/(n_M*F)$$
$$W_A = I_A*t*\mu_A/(n_A*F)$$

Where

W_M, W_A – weights of the deposited metals M and A;
μ_M, μ_A – weights of one mole of the metals M and A;
n_M, n_A - numbers of electrons transferred by the ions M and A;
F – Faraday's constant, **F** = 96485 Coulombs;
t - time.

Then the composition of the deposited alloy (molar concentration of **A**):

$$C_A = I_A/(I_M n_A/n_M + I_A n_A/n_A)$$

Under equilibrium conditions ions of a metal start to deposit on the cathode surface when its potential is brought below the electrode potential calculated according to the Nernst equation. In the real process the cathode potential, at which the deposition starts is even below the equilibrium Nernst potential due to the electrode Polarization.

If the electrode potentials of the alloy components are different ($E_M > E_A$) then the following conditions are possible:

- $E_c > E_M > E_A$ (E_c is the cathode potential). Under these conditions no reduction reactions occur. No electric current is passing through the electrolyte.
- $E_A < E_c < E_M$. Only **M** is deposited. The electric current is a result of the reaction $M^{n+} + ne^- = M$.
- $E_c < E_A < E_M$. Both **M** and **A** are deposited but the deposition of **M** is preferable. The electric current is a result of the both reactions: $M^{n+} + ne^- = M$ and $A^{n+} + ne^- = A$.

8.3.2 Effect of complexing agent

Electroplating of an alloy composed of metals with different Electrode potentials (more noble metal and more active metal) results in preferential deposition of the metal with higher potential (more noble metal).In order to obtain an alloy with the composition similar to the ratio of the metals contents in the electrolyte their potentials should be brought closer together.**Complexing (chelating)** is a method of approximating (getting closer) electrode potentials of the different metals in the electrolyte by converting the simple ions of more noble metal into complex ions with lower potential. **Complexing agent (chelating agent)** is a substance used for complexing particular ions in the electrolyte. Ions of the complexing agent bind the simple metal ions forming complex ions.Complexing agent not only approximates the metals potentials but it also retains the more noble ions in the solution preventing their immersion deposition.
In order to achieve more stable effect complexing agent is commonly added to the electrolyte solution in an amount higher than it is required by the stoichiometric composition. The complexing agent in non-binded form is called **free complexing agent**.A complexing agent may affect on only one of the metals shifting its electrode potential to the negative side when the second metal stays in form of simple ions.When a complexing agent form complexes with both metal ions potentials of both of them are shifted to the negative side but the difference between them decreases (they are getting closer).

Examples of complexing agents:

- Potassium cyanide: **KCN**
- Potassium tartrate: $\mathbf{K_2C_4H_4O_6}$
- Potassium sodium tartrate (Seignette's salt or Rochelle salt): $\mathbf{KNa_2C_4H_4O_6 \cdot 4H2O}$
- Methanesulfonic acid: $\mathbf{CH_3SO_3H}$
- Amino acids
- Phosphoric acid: $\mathbf{H_3PO_3}$
- Citric acid: $\mathbf{C_6H_8O_7}$
- Thiourea: $\mathbf{(NH_2)_2CS}$

8.3.3 Effect of operating parameters

- **Electric current density**. Commonly increase of current density results in **increase of the content of the less noble metal** in the deposited alloy.
- **Temperature**. Increase in temperature causes decrease of the cathode Polarization. Activation polarization decreases due to

NOTE

intensification of the gaseous Hydrogen formation. Concentration polarization drops as a result of increase of the metal concentration in the Diffusion layer at the cathode surface. Lower cathode polarization at increased temperature results in **increase of the content of the more noble metal** in the alloy.

- **Agitation**. Agitation reduces the thickness of the cathode Diffusion layer, which causes decreased concentration polarization. Lower cathode polarization in agitated cathode or electrolyte results in **increase of the content of the more noble metal** in the alloy.
- **Additives (addition agents)**. Additives (brighteners, levelling agents) act similar to complexing agents causing **increase of the less noble metal** in the alloy. Addition agents are most effective in the electrolytes containing simple (non-comlexed) metal ions.

8.3.4 Brass plating

The yellow brass deposits obtained by plating of copper and zinc alloy in proper ratio produces smooth finish and generally three types of bath are employed. They are cyanide brass plating, rapid plating baths and pyrophosphate brass plating.

Cyanide brass plating composition

Copper cyanide	- 31 g /l
Zinc cyanide	- 12.5 g /l
Total cyanide	- 43 g/ l
Anode	- Brass & Zinc

8.4 Brush Plating

Brush plating is an electroplating process performed with a hand tool rather than a tank of coating solution. The brush plating processes are also called as contact plating, selective plating, swab plating or electrochemical metallizing processes. During plating the metal to be coated is connected cathodically to the current source. The plating is then applied by means of a brush or swab, soaked with solutions and connected to a flexible anode cable.

8.5 Cladding

Cladding is the bonding together of dissimilar metals. Cladding refers to the metallurgical process of coating a metal onto another metal under high temperature and pressure so as to protect the inner metal from corrosion. It is often achieved by extruding two metals through a

die as well as pressing or rolling sheets together under high pressure. Cladding may be done with different methods such as Laser cladding, Plasma cladding, Roll bonding and Explosive cladding.

8.5.1 Laser cladding

It is a method of depositing material by which a powdered or wire feedstock material is melted and consolidated by use of laser in order to coat part of a substrate. Laser cladding uses the high energy density generated by a laser beam to form a molten pool in a base material for metallurgically bonding with a filler material using a diffusion type of weld. In laser cladding, the laser beam is defocused on the work piece with a selected spot size. The powder coating material is carried by an inert gas through a powder nozzle into the melt pool. The laser optics and powder nozzle are moved across the work piece surface to deposit single tracks, complete layers or even high-volume build-ups.

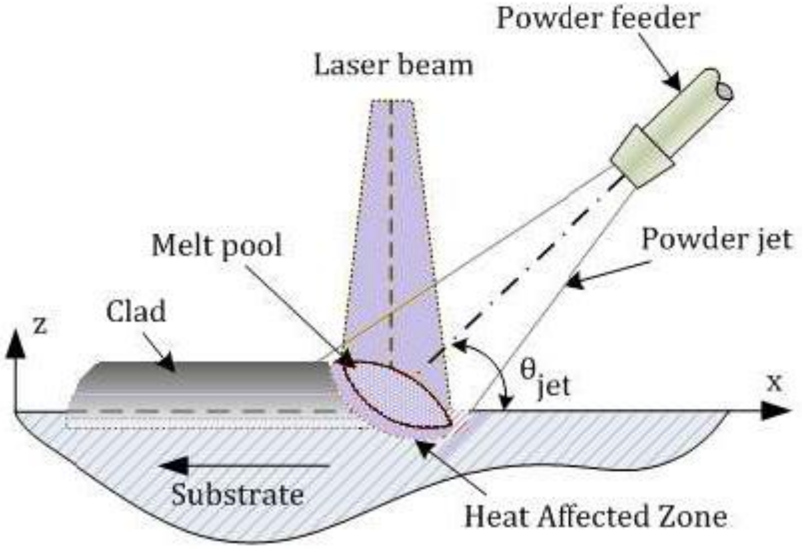


Figure 8.2 Laser Cladding

8.5.2 Plasma Cladding

Plasma cladding machine built according to customer's demand, built for the repair of ones. This machine does not only include cladding; it is also designed to be closely linked three dimensional CAD software allows to tailor the best pattern before any production. The fully automated 6 axes CNC machine will then guarantee that parts up to 15 m can be cladded with the highest quality standard. In many types of industrial machinery, surface damage generated by sliding or abrasive wear limits the life of the components and therefore reduces their durability and reliability.

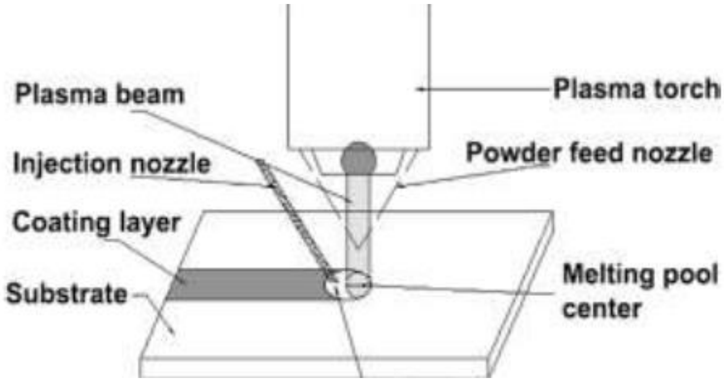


Figure 8.3 Plasma Cladding

This drives the development of wear-resistant coatings and films that enable to improve the performance of engineering components under different conditions. Low heat input keeps dilution to a minimum and the alloy maintains optimum wear-resistant properties. The heat affected zone is very thin under the surface and part distortion is avoided. Homogeneous coating deposition occurred with a constant and controlled quality.

8.5.3 Roll Bonding

Roll bonding is a solid state, cold welding process, obtained through flat rolling of sheet metals. In roll bonding, two or more layers of different metals are passed through a pair of flat rollers under sufficient pressure to bond the layers. The pressure is high enough to deform the metals and reduce the combined thickness of the clad material. The mating surfaces must be previously prepared (scratched, cleaned, degreased) in order to increase their friction coefficient and remove any oxide layers. The process can be performed at room temperature or at warm conditions. Heat may be applied in order to improve the ductility of metals and improve
the strength of the weld. The applications of roll bonding can be used for cladding of metal sheets, or as a sub-step of the accumulative roll bonding. Bonding of the sheets can be controlled by painting a pattern on one sheet; only the bare metal surfaces bond and un-bonded portion can be inflated if the sheet is heated and the coating vaporizes. This concept is used to make heat
exchangers for refrigeration equipment.

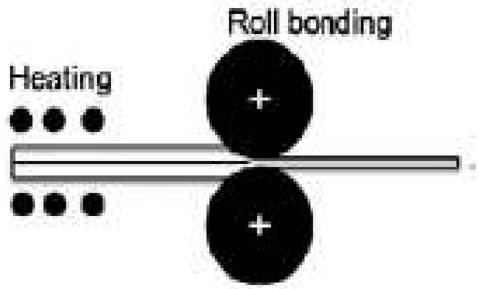


Figure 8.4 Roll Bonding

8.5.4 Explosive Cladding

Explosive cladding is also known as explosion welding. It is the bonding of two or more dissimilar of explosives. It is accomplished by a high-velocity oblique impact between two metals. The impact produces sufficient energy to cause the colliding metal surfaces to flow hydro intimately contact one another in order to promote solid-state bonding. The metal surfaces under high pressure from the explosion, and an atomistic bonding occurred between the dissimilar metals. Explosive cladding is a pressure weld process at room temperature.

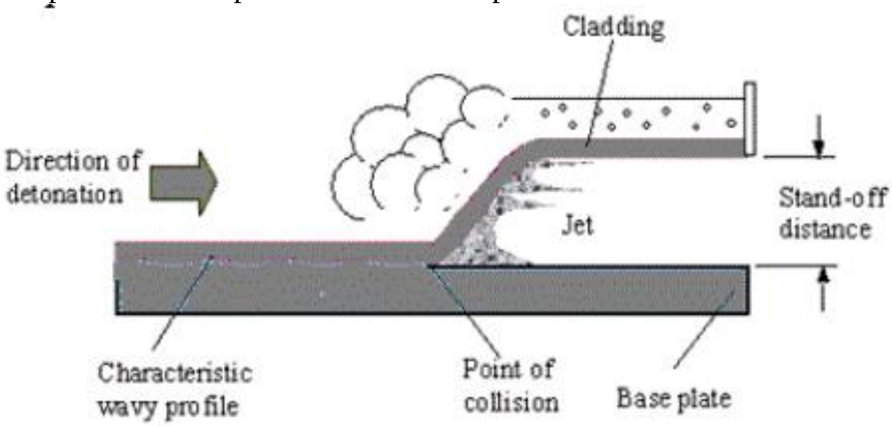


Figure 8.5 Explosive cladding

8.6 Vapour Deposition

Vapour deposition is of two types

- Chemical vapour deposition (CVD)
- Physical vapour deposition (PVD)

8.6.1 Chemical Vapour Deposition (CVD)

CVD involves the dissociation and/or chemical reactions of gaseous reactants in a activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogeneous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity

NOTE

of a heated surface leading to the formation of powders or films, respectively. Though CVD has been used to produce ultrafine powders, this review article is mainly concerned with the CVD of films and coatings. Fig. 1 shows a schematic diagram of CVD of coatings. CVD is a relatively mature technique. The formation of soot due to incomplete oxidation of firewood since prehistoric times is probably the oldest example of deposition using CVD. The CVD process was developed as an economically viable industrial process in the field of extraction and pyrometallurgy for the production of high purity refractory metals such as Ti, Ni, Zr and Ta.

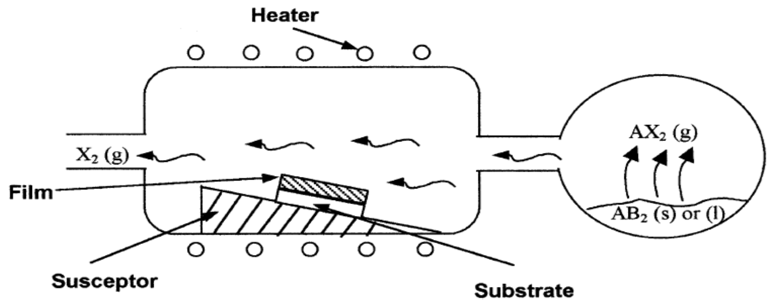


Figure 8.6 Chemical Vapour Deposition (CVD)

8.6.2 Physical vapour deposition (PVD)

Physical vapour deposition is a complex process which involves the laser ablation of a target material and the deposition via nucleation and film growth of the ablated material onto a substrate. The individual steps are vital for the final film crystallinity and stability. PVD deposition can also be used to create multicomponent stoichiometric films from one target. PVD can be used to synthesize metastable materials which would otherwise with standard techniques, be difficult to fabricate.

8.7 Check your progress questions

1. Give any four application of electroforming process.
2. Explain about brush plating
3. What is cladding?
4. Explain in detail about the process of CVD

8.8 Answers to check your progress questions

1. Electroforming is a process for making metallic articles with good dimensional stability

Complex shaped objects are finished easily

Making of moulds

Decorative coat

2. Brush plating is an electroplating process performed with a hand tool rather than a tank of coating solution. The brush plating processes are also called as contact plating, selective plating, swab plating or electrochemical metallizing processes. During plating the metal to be coated is connected cathodically to the current source.

3. Cladding refers to the metallurgical process of coating a metal onto another metal under high temperature and pressure so as to protect the inner metal from corrosion.

4. CVD involves the dissociation and/or chemical reactions of gaseous reactants in a activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogeneous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated surface leading to the formation of powders or films, respectively. Though CVD has been used to produce ultrafine powders, this review article is mainly concerned with the CVD of films and coatings. Fig. 1 shows a schematic diagram of CVD of coatings.

8.9 Summary

- An alloy coating may be obtained by a co-deposition of the alloy constituents from the electrolyte containing their ions. Deposited alloys may possess properties and combination of properties, which ate not achievable in the coatings of pure metals. Electroplating allows to prepare alloys, which cannot be produced by melting. Some metals may be deposited only in form of their alloys. For example electroplating molybdenum (**Mo**), germanium (**Ge**) or tungsten (**W**) is possible only from the electrolytes containing also ions of iron (**Fe**) or nickel (**Ni**).
- Brush plating is an electroplating process performed with a hand tool rather than a tank of coating solution. The brush plating processes are also called as contact plating, selective plating, swab plating or electrochemical metallizing processes. During plating the metal to be coated is connected cathodically to the current source. The plating is then applied by means of a brush or swab, soaked with solutions and connected to a flexible anode cable.
- Cladding is the bonding together of dissimilar metals. Cladding refers to the metallurgical process of coating a metal onto another metal under high temperature and pressure so as to protect the inner metal from corrosion. It is often achieved by extruding two metals through a die as well as pressing or rolling sheets together

NOTE

under high pressure. Cladding may be done with different methods such as Laser cladding, Plasma cladding, Roll bonding and Explosive cladding.

8.10 Keywords

Complexing (chelating) is a method of approximating (getting closer) electrode potentials of the different metals in the electrolyte by converting the simple ions of more noble metal into complex ions with lower potential.

The complexing agent in non-binded form is called **free complexing agent.**

Electric current density, Commonly increase of current density results in **increase of the content of the less noble metal** in the deposited alloy.

Explosive cladding is also known as explosion welding. It is the bonding of two or more dissimilar of explosives

8.11 Self-assessment questions and exercises

1. Explain about PVD process
2. Discuss the process of laser cladding
3. Write the advantages of electroforming method.
4. What is brush plating?

8.12 Further readings

1. Metal Finishing Handbook, Elseveit, The Netherlands, 2005.
2. Jack W. Dini, Electrodeposition - The Materials Science of Coating and Substrates Noyes Publications, New York,1993.
3. Jason P Welsh, Electroforming for Beginners, Electroforming Series, 2018

Unit-9: Electroless Plating

Structure

9.0 Introduction

Electroless plating is a method of plating metal by chemical reaction. The piece to be plated is immersed in a reducing agent which changes metal ions to metal that forms a deposit on the piece. Electroless plating provides uniformity of the deposits, even on complex shapes. Deposits are often less porous and thus provide better barrier corrosion protection to steel. Deposits can be plated with zero or compressive stress. Deposits have inherent lubricity and non-galling characteristics, unlike electrolytic nickel. Deposits have good wet ability for oils.

9.1 Objective

After going through this unit you are able to

- Know about the versatility of electroless plating
- Understand the concept of anodizing
- Appreciate the process of composite coating

9.2 Principle advantages and limitation of Electroless Plating

Electroless plating is a technique of depositing a noble metal (from its salt solution) on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy. The added reducing agent causes the reduction of the metallic

ions to metal, which eventually gets plated over the catalytically activated surface giving a highly uniform, but thin coating. Thus:

Metal ions + Reducing agent → Metal + Oxidised product (s)

Deposited over catalytically active surface

The driving force is autocatalytic redox reaction on pretreated catalytic surface. These develops pore easily and further diffusion of gases is possible. The cost of the process is high and subjected to corrosion easily.

9.2.1 Preparation of active surface of the object to be plated

This step is most important in this technique. This is achieved by using one of the following methods:

i. Etching,
ii. Electroplating a thin layer of the metal to be plated or any other suitable metal. This is usually followed by heat treatment.
iii. Treating with stannous chloride, followed by dipping in palladium chloride solution. This treatment yields a thin layer of Pd on the treated surface. Usually, this is followed in case of plastics and printed circuit boards.

9.2.2 Plating bath

i. Soluble salt of metal (like chloride or sulphate) to be plated.
ii. Reducing agent like formaldehyde, hypophosphite, etc.
iii. Complexing agent like tartarate, citrate, succinate, etc. This improves the quality of the deposit.
iv. Exaltant like succinate, fluoride, glycinate, etc. This enhances the plating rate.
v. Stabilizer like thiourea, cations of lead, calcium, thalium, etc. is added to prevent the decomposition of the plating bath solution.
vi. Buffer like sodium acetate, sodium hydroxide + rochelle salt, etc. is added to control the pH of the bath. It may be

pointed that pH of the bath plays a "critical role" in getting a uniform, but thin deposit.

Advantages of electroless plating: (i) No electrical energy is required. (ii) Better throwing power. (iii) Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out. (iv) Even intricate parts (of irregular shapes) can be plated uniformly. (v) Electroless plated coatings possess unique mechanical, chemical and magnetic features.

9.2.3 Limitations

- The process is more expensive
- The stipulated maintenance of temperature is required to favour catalytic process

9.3 Composite coating mechanism and application

A composite coating is the plating of material of choice in ceramic bath called metal matrix composites.

Encapsulation mechanism

The positively charged particle is brought to the cathode by electrophoresis. These particles keeps on surronding the cathode and at one stage the deposition becomes strong.

Application

Automobile disk brakes, sports car and tank armours are prepared by this method.

9.4 Anodizing

Anodized coatings are, generally, produced on non-ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process, in which the base metal is made as anode. It is carried out by passing a moderate direct electric current through a bath in which the metal or alloy is suspended from anode. The bath, usually, contains sulphuric, chromic, phosphoric, oxalic or boric acid. As the anodized coatings are somewhat thicker than the natural oxide films, so they possess improved resistance to corrosion as well as mechanical injury. Aluminium coatings are formed by electrolysis in a suitable acid electrolyte (sulphuric, chromic, oxalic or phosphoric acid) at moderate temperatures (about 35 to 40°C) and moderate current densities. The coating forms as a result of progressive oxidation, starting at the aluminium surface. An oxide film, initially very thin, grows from the metal surface outwards and increases in thickness as oxidation continues at aluminium anode. The outer part of the oxide film formed is very porous and considerably softer than the layer directly adjoining the metal surface. The minute exposed pores can be made more corrosion-resistant by the process of sealing, which consists of exposing film to boiling water. This treatment changes porous

alumina at the surface of coating into its monohydrate ($Al_2O_3.H_2O$), which occupies more volume, thereby the pores are sealed. Alternatively, sealing can be done by immersion of the film in boiling dilute sodium dichromate solution.

9.5 Types of anodizing bath

Sulphuric acid bath

Sulphuric acid is the most widely used solution to produce anodized coating. Coatings by moderate thickness are known as Type II. Sulphuric acid bath producing hard anodizing layers are classified as type – III. It is also called hard coat (or) engineering anodizing.

Organic acid bath

Anodizing can be carried out in carboxylic acids such as oxalic acid to produce integral colours in the anodized coating without dyes. Desirable thickness upto 50 microns are achieved using this bath.

Borate and Tartarate Baths

Anodizing can also be performed in borate (or) tartarate baths in which aluminium oxide is insoluble. Thickness of the obtained coat is varies linearly with applied potential. The surface finish by these bath are very smooth as compared to other bath processes.

9.6 Colourizing of anodizing aluminium

Coloured coatings on metal surfaces continue to be a growth technology for decorative, protective and functional applications. New colouring processes are being formulated for anodised aluminium to meet the demands for architectural and solar applications. Anodising is an electrochemical process of producing an oxide film over the surface of aluminium by passing a current at sufficient voltage through a suitable electrolyte using aluminium as the anode and lead or graphite or stainless steel as the cathode. The widely used anodising electrolyte is sulphuric acid. Anodising may be regarded as the artificial thickening of the thin (1–5 nm) native oxide film that is always present on aluminium exposed to the atmosphere. When an electric current is passed through the cell, the aluminium surface is converted into an adherent aluminium oxide coating, which is integral with the aluminium substrate. The film formed consists of a thin barrier layer beside the metal, depending upon the nature of the electrolyte, and a thick porous layer over the barrier layer. The porous nature of the anodic coating is advantageously used to incorporate dyes, pigments, corrosion inhibitors or lubricants. Colouring

of anodised aluminium is carried out by organic colouring, electrolytic colouring and integral colour anodising. In the organic colouring process, colouring takes place by the adsorption of the dye in the outer portion of the pores. Very light fast shades of bronze or black were obtained from the electrolyte system containing either Ni or Tin salts by electrodeposition of fine Ni or Tin particles in the pores of conventionally produced oxide films. Electrolytic colouring of anodised aluminium by direct current gives faster and greater yield.

9.7 Check your progress question

1. What is organic acid bath?
2. Explain the process of anodizing
3. Give the limitations of electroless plating
4. Write the composition of plating bath in electroless plating

9.8 Answers to check your progress questions

1. Anodizing can be carried out in carboxylic acids such as oxalic acid to produce integral colours in the anodized coating without dyes.

2. It is carried out by passing a moderate direct electric current through a bath in which the metal or alloy is suspended from anode. The bath, usually, contains sulphuric, chromic, phosphoric, oxalic or boric acid. As the anodized coatings are somewhat thicker than the natural oxide films, so they possess improved resistance to corrosion as well as mechanical injury. Aluminium coatings are formed by electrolysis in a suitable acid electrolyte (sulphuric, chromic, oxalic or phosphoric acid) at moderate temperatures (about 35 to 40°C) and moderate current densities. The coating forms as a result of progressive oxidation, starting at the aluminium surface.

3. Electroless plating gets plated over the catalytically activated surface giving a highly uniform, but thin coating. These develops pore easily and further diffusion of gases is possible. The cost of the process is high and subjected to corrosion easily.

4. Soluble salt of metal (like chloride or sulphate) to be plated.Reducing agent like formaldehyde, hypophosphite, etc.Complexing agent like tartarate, citrate, succinate, etc. This improves the quality of the deposit.Exaltant like succinate, fluoride, glycinate, etc. This enhances the plating rate. Stabilizer like thiourea, cations of lead, calcium, thalium, etc. is added to prevent the decomposition of the plating bath solution.

NOTE

9.9 Summary

- **Electroless plating** is a technique of depositing a noble metal (from its salt solution) on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy. The added reducing agent causes the reduction of the metallic ions to metal, which eventually gets plated over the catalytically activated surface giving a highly uniform, but thin coating.
- Anodized coatings are, generally, produced on non-ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process, in which the base metal is made as anode. It is carried out by passing a moderate direct electric current through a bath in which the metal or alloy is suspended from anode.
- Coloured coatings on metal surfaces continue to be a growth technology for decorative, protective and functional applications. New colouring processes are being formulated for anodised aluminium to meet the demands for architectural and solar applications.

9.12 Keywords

A composite coating is the plating of material of choice in ceramic bath called **metal matrix composites**.

Anodizing can be carried out in carboxylic acids such as oxalic acid to produce integral colours in the anodized coating **without dyes**. Desirable thickness upto 50 microns are achieved using this bath.

Exaltant like succinate, fluoride, glycinate, etc. This enhances the plating rate.

9.11 Self assessment question and exercise

1. Explain the process of colourizing aluminium.
2. Give the mechanism of composite coating process.
3. What is anodizing?
4. How surfaces are to be prepared for electroless process.

9.12 Further Reading

1. Jack W. Dini, Electrodeposition - The Materials Science of Coating and Substrates Noyes Publications, New York,1993.
2. Frederick A. Lowenheim Electroplating: Fundamentamental of metal finishing Mcgraw Hill, New York, 1978.

3. Glenn O Mallory and Juan B Hajdu, Electroless plating : Fundamentals and Applications, American Electroplaters and Surface Finishers Society, Orlando, Fla,1990.

NOTES

NOTE

Block-4: Nanomaterials Characterization Techniques and Computer applications in Chemistry

Unit-10: Nanomaterials

Structure

10.0 Brief introduction to Nanoscience and Technology

NanoTechnoogy is the engineering of functional system at the molecular scale. The word nano means dwarf. Nano Tecnology and Science have been growing rapidly. It (sometimes shortened to nanotech) is the technique of manipulating the matter on an atomic and molecular level having scale and size in the nanometer range. Generally, it deals with structures sized between 1 to 100 nanometers, in at least one dimension and involves developing materials or devices possessing at least one dimension within that size. It is important to note that at such a scale/ and Quantum mechanics , dealing with dual nature and interaction of matter and energy, becomes very important.

The important difference between nano science and nano technology is that former is related to the study of relationship between various phenomena, physical properties and material dimensions at nano scale, whereas later is application of these nano structures and principles behind them to make scale devices and materials. An important aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials, which makes possible new quantum mechanical effects. As material size reduces from centimeter(bulk) to nanometer scale, properties mostly decrease as much as six orders of magnitude to that at macro level. The change is due to the nature of interactions among the atoms that are averaged out of existence in the

bulk material. The same can be explained in another way i.e surface energy increases with the overall surface area which in turn strongly dependent on the dimension of material. As nanostructures are having reduced dimensions, it leads to increase in surface energy via increase in surface area. The change in properties from macro scale to nano scale can be observed by taking a simple example as given below. The change in properties from macro scale to nano scale can be observed by taking a simple example as given below.

NOTES

Let us take an imaginary cube of gold 3 feet on each side. It is sliced in half along its length, width and height to produce eight little cubes, each 18 inches on a side. If we continue cutting the gold in this way from inches to centimeters , from centimeters to millimeters and from millimeters to microns. We still notice no change in properties of gold between each stage except cash value and weight. All gold cubes are soft, shiny, yellow and having same melting point. But when these um size gold particles µm size gold particles are further sliced into nanosize particels, every thing will be changed including gold's colour,melting point and chemical properties. Melting point of nano gold is less than that of bulk gold melting point.

Similarly instead of yellow colour, nano gold particles appear in different colour. This colour depends on the size of the particle. Not only for gold, all the materials will show the peculiar behavior and change in their properties when they enter into the nano scale. That is why one nanometer is called s magical point on the dimension scale. One example is the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials are a subject of nano mechanics research. Catalytic activities also reveal new behavior in the interaction with biomaterials. Thus manipulation of matter at nanoscale provides some novel properties to the material. Nanotechnology can be thought of as externsions of tradional disciplines towards the explicit considerations of these special properties. The traional disciplines of physics and chemistry can be re-interpreted as specific applications of nanotechnology. Broadly speaking, nanotechology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

10.1 Objectives

After going through this unit you are able to

- Understand the basics of nano science

NOTE

- Know the Strength of molecular dimensions in various fields
- Appreciate the preparatory procedures of nano particles

10.2 Preparatory synthesis

The various method of preparing nano particles is discussed here,

10.3 Sol-gel method

Sol-gel process is a wet chemical technique(also known as chemical solution deposition) widely used and is applied in material science and ceramic engineering. Such methods are used primarily for the fabrication of materials typically a metal oxide) starting from a chemical solution(sol) which acts as the precursor for an integrated network(or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension (or dispersion) – a system composed of discrete (often amorphous) submicrometer particles dispersed to various degrees in a host fluid. Formation of a metal oxide involves connecting the metal conters with odo(M-O-M) or hydroxo(M-OH-M) bridges, therefore generating metal-oxo or metal-hydoxo polymers in solution. Thus the sol evolves towards the formation of a gel like diphasic system containing both a liquid phase and solid phase whose morphologies range for discrete particles to continuous polymer networks.

Following process is removal of the remaining liquid (solvent) phase which requires a drying process, leading to significant amount of shrinkage and destination. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. Afterwards, a thermal treatment or firing process is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. The precursor sol can be either deposited on a substrate to form a film(e.g by dip coating or spin-coating), cast into a suitable container with the desired shape(e.g to obtain a monolithic ceramics, glasses, fibres, membranes. Aerogels) or used to synthesize powders (e.g microsphers, nanospheres)

The sol gel technique is a long-established industrial process for the generation of colloidal nanoparticles from liquid phase for the production of advance nanomaterials and coatings. It refers to the hydrolysis and condensation of alkoxides –based precursors such as Si(OEt)4(tetraethyl orthosiliate or TEOS). The reactions involved in

the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)z can be described as follows:

MOR + H_2O → MOH +ROH(hydrolysis)

MOH+ ROM → M-O-ROH(condensation)



Sol-gel process can be characterized by a series of distinct steps:

Step 1: Formatio of different stable solutions of the alkoxide or solvated metal precursor (the sol)

Step 2: Gelation resulting from the formation of an oxide or alcohol bridged network(the gel)by a polycondensation or polyesterification reaction that results in a dramatic increase in the viscosity of the solution.

Step 3: Aging of the gel(Synersis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening(also referred t as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transormations may occur concurrently with syneresis . The Aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

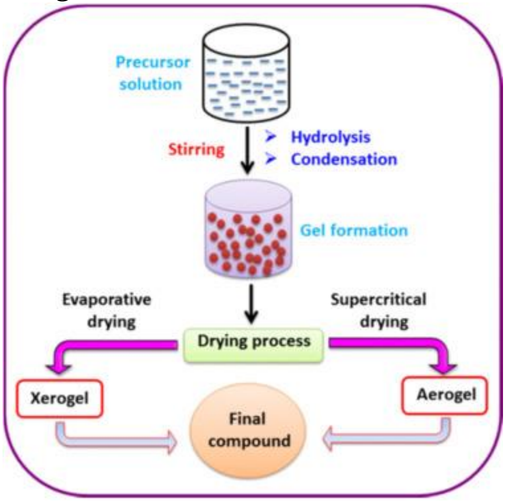
Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in te structure of the gel. The drying process has itself been broken tonto four distinct steps: (i) the constant rate period (II) the critical point (III) the falling rate period (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed as xeroge. If the solvent(such as water) is extracted under supercritical or near super critical condtions, the product is an aerogel.

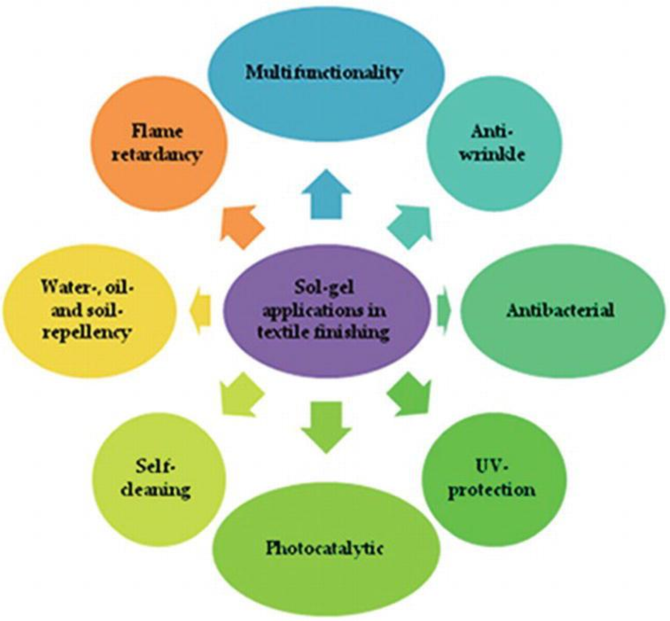
Step 5: Dehydration , during which surface bound M-OH groups are removed there by stabilizing the gel gainst rehydration. This is normally achieved by calcining the monolith at temperatures upto 800 oC

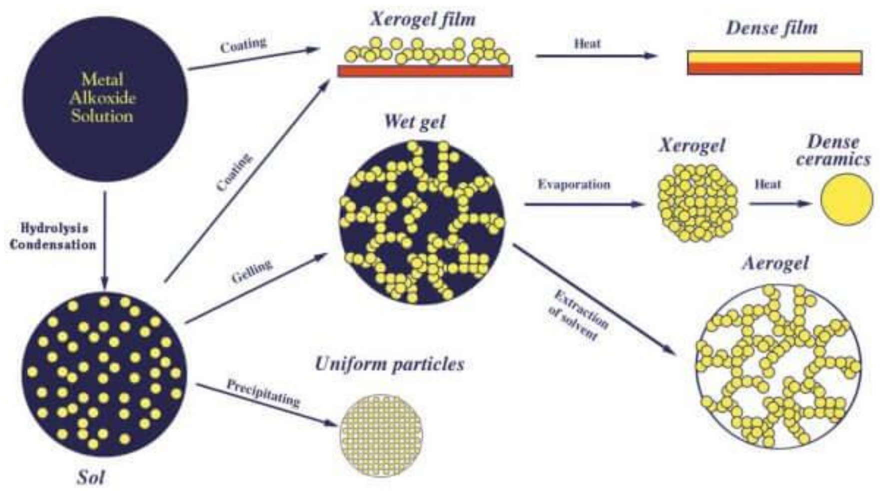
Step 6: Densification and decomposition of the gels at high temperature (T>800 oC). The Pores of the gel network are collapsed and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

Applications of sol-gel

Sol-gel derived material have diverse applications in optics, electronics,energy, space (bio) sensors, medicine (e.g) controlled drug release) reactive material and separation (e.g chromatography) technology. They offer unique opportunities for access to organic-inorganic materials.







10.4 Thermolysis

The thermolysis process is the thermal decomposition of materials in an oxygen-free environment and requires an input of heat energy, pressure and pre-determined temperature depending on the material to be pyrolized as nano particle. Based on the applied heat andmaterial under use size dependent nano particles of metal oxides are prepared.

10.5 Combustion method

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. It is not an easy task to produce nanomaterials by conventional SHS, where the typical scale of heterogeneity for the initial solid reactants is on the order of 10–100 lm. However, several methods were suggested for synthesis of nanomaterials by using this approach: (i) SHS synthesis, followed by intensive milling; (ii) SHS + mechanical activation (MA); (iii) SHS synthesis followed by chemical treatment, so-called chemical dispersion; (iv) SHS with additives; (v) carbon combustion synthesis (CCS). The desirable particle sizes are obtained by this method.

10.6 Solvothermal synthesis

It is a method of producing nano materials as similar to the hydrothermal route.The only difference being that the precursor solution is usually non-aqueous. Using the solvothermal route gains one the benefits of both the sol-gel and hydrothermal routes. Thus,

solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of metal oxide nanoparticles or nanostructure products. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type.Solvothermal synthesis has been used in laboratory to make nanostructured titanium dioxide, graphene, carbon spheres, chalcogenides and other materials.

10.7 Microemulsion method

Uniform and size controllable silver NPs can be synthesized using microemulsion techniques. The NPs preparation in two-phase aqueous organic systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. The interface between the two liquids and the intensity of inter-phase transport between two phases, which is mediated by a quaternary alkyl-ammonium salt, affect the rate of interactions between metal precursors and reducing agents. Metal clusters formed at the interface are stabilized, due to their surface being coated with stabilizer molecules occurring in the non-polar aqueous medium, and transferred to the organic medium by the inter-phase transporter. One of the major disadvantages is the use of highly deleterious organic solvents.

Thus large amounts of surfactant and organic solvent must be separated and removed from the final product. For instance, researchers had used dodecane as oily phase (a low deleterious and even nontoxic solvent), but there was no need to separate the prepared silver solution from the reaction mixture. On the other hand, colloidal NPs prepared in nonaqueous media for conductive inks are well-dispersed in a low vapor pressure organic solvent, to readily wet the surface of polymeric substrate without any aggregation. The advantages can also be found in the applications of metal NPs as catalysts to catalyze most organic reactions, which have been conducted in non-polar solvents. It is very important to transfer metal NPs to different physicochemical environments in practical applications.

10.6 Check your progress questions

1. What is thermolysis process?

2. Explain in detail about microemulsion method.

3. Give the applications of sol-gel method.

4. Discuss the advantages of solvothermal method.

10.7 Answers to check your progress questions

1. The thermolysis process is the thermal decomposition of materials in an oxygen-free environment and requires an input of heat energy, pressure and pre-determined temperature depending on the material to be pyrolized as nano particle. Based on the applied heat andmaterial under use size dependent nano particles of metal oxides are prepared.

2. Uniform and size controllable silver NPs can be synthesized using microemulsion techniques. The NPs preparation in two-phase aqueous organic systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. The interface between the two liquids and the intensity of inter-phase transport between two phases, which is mediated by a quaternary alkyl-ammonium salt, affect the rate of interactions between metal precursors and reducing agents. Metal clusters formed at the interface are stabilized, due to their surface being coated with stabilizer molecules occurring in the non-polar aqueous medium, and transferred to the organic medium by the inter-phase transporter. One of the major disadvantages is the use of highly deleterious organic solvents.

3. Sol-gel derived material have diverse applications in optics, electronics,energy, space sensors, medicine reactive material and separation) technology. They offer unique opportunities for access to organic-inorganic materials.

4. Using the solvothermal route gains one the benefits of both the sol-gel and hydrothermal routes. Thus, solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of metal oxide nanoparticles or nanostructure products.

10.9 Summary

- NanoTechnoogy is the engineering of functional system at the molecular scale. The word nano means dwarf. Nano Tecnology and Science have been growing rapidly. It (sometimes shortened to nanotech) is the technique of manipulating the matter on an atomic and molecular level having scale and size in the nanometer range. Generally, it deals with structures sized between 1 to 100 nanometers, in at least one dimension and involves developing materials or devices possessing at least one dimension within that size. It is important to note that at such a scale/ and Quantum mechanics , dealing with dual nature and interaction of matter and energy, becomes very important.

- Sol-gel process is a wet chemical technique(also known as chemical solution deposition) widely used and is applied in material science and ceramic engineering. Such methods are used primarily for the fabrication of materials typically a metal oxide) starting from a chemical solution(sol) which acts as the precursor for an integrated network(or gel) of either discrete particles or network polymers.
- The thermolysis process is the thermal decomposition of materials in an oxygen-free environment and requires an input of heat energy, pressure and pre-determined temperature depending on the material to be pyrolized as nano particle. Based on the applied heat andmaterial under use size dependent nano particles of metal oxides are prepared.
- Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. It is not an easy task to produce nanomaterials by conventional SHS, where the typical scale of heterogeneity for the initial solid reactants is on the order of 10–100 nm.

10.9 Keywords

Solvothermal Synthesis is a method of producing nano materials as similar to the hydrothermal route.

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials.

10.10 Self-assessment questions and exercises

1. What are nano particles?
2. Explain in detail about sol-gel method.
3. Give the advantages of thermolysis process.
4. Write a note on combustion method.

10.10 Further reading

1. G. Cao , Nanostructures and nanomaterials- Synthesis, properties and applications, Imperial College Press 2004.
2. P.Yang (ed.) The chemistry of nanostructured materials, World Scientific 2005
3. C.N.R. Rao, A. Muller, A.K. Cheetam (Eds), The Chemistry of Nanomaterials, Vol.1, 2, Wiley – VCH, Weinheim, 2004.

4. C.P. Poole, Jr: F.J. Owens, Introduction to Nanotechnology Wiley Interscience, New Jersey, 2003
5. Kenneth J. Klabunde (Ed), Nanoscale materials in Chemistry, Wiley-Interscience, New York, 2001
.

NOTES

Unit -11: Physical and Chemical Method of Nanomaterials

Structure

11. 0 Introduction

Nanotechnology is the design of functional materials with characteristic dimensions in nanometers from molecular scale. Such materials and systems can be rationally designed to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size. Phenomena at the nanometer scale are likely to be a completely new world. Important changes in behavior are caused not only by continuous modification of characteristics with diminishing size, but also by the emergence of totally new phenomena such as quantum confinement, a typical example of which is that the color of light emitting from semiconductor nano-particles depends on their sizes. Designed and controlled fabrication and integration of nano-materials and nano devices is likely to be a revolutionary for science and technology. Nanotechnology can provide unprecedented understanding about materials and devices, and is likely to impact many fields. In generally synthesis of nonmaterial's can be classified two types.

1. Bottom-up approach
2. Top-down approach.

In bottom-up approaches include the miniaturization of materials components (up to atomic level) with further self-assembly process leading to the formation of nanostructures. During self-assembly the physical forces operating at Nano scale are used to combine units into larger stable structures. In top-down approaches use larger initial structures, which can be externally controlled in the processing of nanostructures.

11.1 Objectives

After going through this you are able to

- Understand the types of nano particle synthesis
- Know the significance of physical method synthesis
- Acquire information about chemical method of nano particle synthesis

11.2 Physical methods

Evaporation condensation and laser ablation are the important physical methods of preparing nanoparticles. The absence of solvent contamination and the uniformity distribution of nanoparticles (NPs) distribution in the prepared film are the advantages of physical synthesis over chemical processes.

11.3 Vacuum Evaporation

Vacuum evaporation is otherwise called as vacuum deposition and vaporization. In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum . The vaporization source is the one that vaporizes materials by thermal processes. The process is carried out at pressure of less than 0.1 Pa and in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C.. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is fairly high. Vapor phase nucleation can occur in dense vapor cloud by multibody collisions. The atoms are passed through a gas to provide necessary collision and cooling for nucleation. These particles are in the range of 1 to 100 nm and are called ultra fine particles or clusters]. The advantages associated with vacuum deposition process are high deposition rates and economy. However, the deposition of many compounds is difficult. Nanoparticles produced from a supersaturated vapor are usually longer than the cluster.

11.4 Sputtering Technique

Sputtering is a physical vapour deposition technique that has been used fabrication of nano particles. One of the biggest advantages of this technique is that it allows the formation of highly pure and uniform thin films, and it has been developed for sputtering both metal (DC sputtering) and semiconductors (RF sputtering). The technique for sputtering thin films consists in bombarding a metallic plate (target) with ions, usually Ar+ , then allowing the materials to be etched away and deposit onto the desired surface. In order to do so, in a vacuum chamber, at a pressure usually between 0.1 and 10 Pa, a potential difference is applied between the anode (sample) and the cathode (target). The applied voltage accelerates the positive ions that will go to impact on the negatively charged cathode. The kinetic energy carried by the ions transfers to the target material and possess enough energy to eject atoms and small clusters, which are spread in the sputtering chamber. The right pressure operation is a key factor for a successful sputtering. It is common to have magnets installed in sputtering devices; a magnetic field normal to the surface of the target makes the electron move towards the anode on a spiral path, as charged particles are affected by magnetic fields following the Lorentz equation.

11.4.1 Sputtering in liquid

Sputtering in liquid is a quite versatile technique for the synthesis of nanoclusters and nanoparticles, as it allows the usage of a quite broad range of materials as sputtering target, plus, by choosing the monomer (dispersing medium) in a smart way. It’s possible to functionalize the nanoparticles and attain control over the particle composition and size. Sputtering is a vacuum technique that uses ionized gas to detach atoms and clusters from a chosen metal target, meaning that also controlling the composition of the gas present in the chamber can be an effective way to control nanoparticle composition and formation mechanism

11.5 Pulsed laser ablation

The mechanism of laser ablation depends on physical properties of metals and environment medium. Ablation of metal target commences with the sorption of laser beam energy. When the laser beam interacts with the metal target, the heat can generate and the photoionization of the metal target occurs. After that, metal nanoparticles will be released from the metal plate as the different phase that depends on the absorbed energy E and plasma plume expands. Hence, if the duration of laser ablation is

much higher than the laser pulse duration, the ablation depth (La) could be obtained as follows

$$La = E^{2/3}, \; t_a = E^{1/2}$$

where t_a is the time of the ablation process. During laser ablation of metal plates, the plasma plume can be formed with the generation of photon and sound. This phenomenon is confined near the metal plate and the face of the metal plate face in the plasma plume remains at high temperature and high pressure. The formation of metal nanoparticles based on laser ablation of the metal plate can be explained as bubbling of metal molecules. The size and concentration of nanoparticles in the liquid are a function of the phase homogeneity of the material released into the liquid during the ablation of metal target. Hence a variety of particle size and considerable concentration were achieved. The energy transfer to the electron on the surface of metal plates depends on the time duration of high power lasers. Thus femtosecond laser pulses can release the electron from the metal plates faster than the thermal action of electron-photon phenomena. The plasma plume can absorb part of the incoming laser energy when the long laser pulse will be used for ablation of the metal target. The absorption of laser beam increases the temperature of the plasma and favors the atomization of the material contained in the plume and metal target with homogenized charades are observed.

11.6 Chemical Methods

The following are the chemical methods to prepare nano particles

11.7 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin flims. In a typical CVD process, the wafer(substrate) is exposed to one or more volatile precursors,which react and/or decomposed on the substrate surface to produce the desired deposit. CVD consists of activating a chemical reaction between the substrate surface and a gaseous precursor. Activation can be achieved either with temperature(Thermal CVD) or with a plasma(PECVD: Plasma Enhanced Chemical Vapour Deposition). The main advantage is the nondirective aspect of this technology. Plasma allows to decrease significantly the process temperature compared to the thermal CVD process. CVD is widely used to produce carbon nanotubes.

Some of the commonly used examples are as under:

(a) Silicon dioxide

NOTE

Silicon dioxide may be deposited by several different processes. Common source gases include silame and oxygem, dicholorosilane($SiCl_2H_2$) and nitrous oxide(N_2O) or tetrathylorthosilicate(TEOS: $Si(OC2H_5)_4$). The reactions are as follows

$$SiH4 + O2 \longrightarrow SiO_2 + 2H_2$$

$$SiCl_2H_2 + 2N_2O \longrightarrow SiO_2 + 2N_2 + 2HCl$$

$$Si(OC2H5)4 \longrightarrow SiO2 + \text{by-products}$$

The choice of source gas depends on the thermal stability of the substrate: for instance, aluminium is sensitive to high temperature. Silane deposits between 300 and 500 ^oC , dicholorsilane at around 900 ^oC and TEOSbetween 650 ad 750 ^oC resulting in an layer of low temperature oxide (LTO). However, silane produces a lower quality oxide than the other methods(lower dielecric strength, for instance), and it deposits nonconformally. Any of these reactions may be used in LPCVD bt the silane reaction is also done inAPCVD. CVD oxide invariably has lower quality than thermal oxide,but thermal oxidation can only be used in ther earliest stages of IC manufacturing.

Oxide may also be grown with impurities(alloying or "doping").This may have two purposes. During further process steps that occur at high temperature, the impurities may diffuse from the oxide into adjacent layers (most notably silicon) and dope them. Oxides containing 5-15% impurities by mass are often used for this purposes. In addition, silicon dioxide alloyed with phosphorus pentoxide ("P-glass") can be used to smooth out uneven surfaces. P-glass soften and reflows at temperatures above 1000 ^oC. This process requires a phosphorous concentration of at least 6%, but concentrations above 8% can corrode aluminium. Phosphorus is deposited from phosphine gas and oxygen.

$$4PH3 + 5O2 \longrightarrow 2P2O_5 + 6H_2$$

Glasses containing both boron and phosphorus (borophosphosilicate glass,BPSG) undergo viscours flow at lower temperatures: around 850 ^oC is achievable with glasses containing around 5 weight % of both constituents, but stability in air can be difficult to achieve . Phosphorous oxide in high concentrations interacts with ambient moisture to produce phosphoric acid. Crystals of BPO4 can also precipitate from the flowing glass on clooling; these crystals are not readily etched in the standard reactive plasmas used to pattern oxides and will result in circuit defects in integrated circuit manufacturing.

Besides these intentional impurities, CVD oxide may contain by products of the depositions process. TEOS produces a relatively pure oxide, whereas silane intorudces hydrogen impurities and dichlorosilane introduces chlorine.

Lower temperature deposition of silicon dioxide and doped glasses from TEOS using ozone rather than oxygen has also been expllred(350 to 500 ^{o}C). Ozone glasses have excellent conformality but tend to the hygroscopic- that is they absorb water from the air due to the incorporation of silanol(Si-OH) in the glass. Infrared spectroscopy and mechanical strain as a function of temperature are valuable diagnostic tools for diagnosing such problems.

Metals

Some metals(notably aluminium and copper) are seldom or never deposited by CVD. As of 2010, a commercially, cost effective, viable CVD process for copper did not exist, through copper formate, copper (hfac)2,Cu(II) ethyl acetoacetate and other precursors have been used. Copper deposition of the metal has been done mostly by electroplating, in order to reduce the cost. Aluminium can be deposited from tri-isobutyl aluminium(TIBAL), tri ethyl/methyl aluminium(TEA,TMA), or dimethylaluminum hydride(DMAH), but physical vapour deposition methods are usually preferred.

However, CVD processes for molybdenum, tantalum, titanium, nickel and tungsten are used. These metals can form useful silicides when deposited onto silicon. Mo, Ta and Ti are deposited by LPCVD, from their pentachlorides. Nickel, molybdenum and tungsten can be deposited at low temperatures from their carbonyl precursors. In general, for an arbitrary
Metal M, the reaction is as follows:

$$2MCl_5 + 5H_2 \Longrightarrow 2\,M + 10\,HCl$$

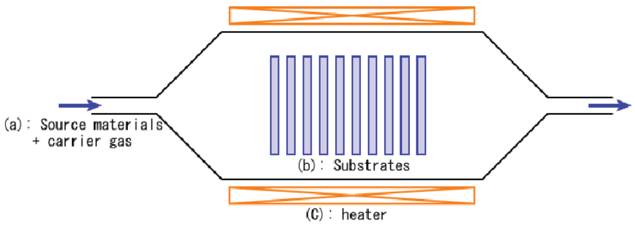
The usual source for tungsten is tungsten hexafluoride , which may be deposited in two ways:

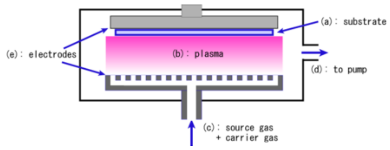
$$WF_6 + 3H_2 \Longrightarrow W + 6HF$$

Types of chemical vapour deposition

Based on difference in the means by which chemical reactions are initiated e.g., activation process) and process conditions number of forms of CVD are in wide used and are frequently referenced in the literature. For example,

NOTE





1. CVD classified by operating pressure can be
    - Atmospheric pressure CVD(APCVD)-CVD processes at atmospheric pressure.
    - Low-pressure(CVD(LPCVD)-CVD processes at sub atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reacions and improce film uniformity across the wafer. Most modern CVD processes are either LPCVD or UHVCVD.
    - Ultra high vacuum CVD(UHVCD)-CVD processes at a very low pressure, typically below 10^{-6} Pa(-10-8 torr). Note that in other fields, alower division between high and ultra-high vacuum is common, often 10^{-7} Pa.
2. CVD classified by physical characteristics of vapour

    - *Aerosal assisted CVD(AACVD)*- A CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique is suitable for used with non-volatile precursors.
    - *Direct liquid injection CVD(DLICVD)*- A CVD process in which the precursors are in liquid form(liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors(typically car injectors). Then the precursor vapours are transported to the substrate as in classical CVD process. This technique is suitable for used on liquid or solid precursors. High growth rates can be reached using this technique.

3. Plasma methods
    - *Microwave plasma-assisted CVD(MPCVD)*
    - *Plasma-Enhanced CVD(PECVD)*-CVD process that utilize plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semicoductors.
    - *Remote plasma enhanced CVD(RPECVD)*-Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.

Methods to produce nanoparticles from atoms are chemical processes based o transormations in solution e.g., sol-gel processing , Chemical Vapour Deposition (CVD),plasma or flame spraying synthesis, laser pyrolysis, atomic or molecular condensation some of which have been briefly mentioned above being common to both approaches.

11.8 Chemical Solution Deposition (CSD)

CSD is a materials growth technique from precursor chemical solution of inorganic or organic metal salts dissolved in organic or water in stoichiometric ratios. The solutions are deposited on a substrate using spin coating, dip coating, web coating, ink jet printing, etc., depending on the requisites. The film thickness can be easily controlled by varying salts concentration based on the employed deposition technique. After the deposition, the solutions are dried and the chemical precursors are pyrolyzed to amorphous or nanocrystalline porous solid with well-defined thickness. CSD can also be used to prepare self-assembled nanostructures using ultradiluted solutions and nanocomposite films which are prepared using colloidal solutions with prepared nanoparticles. CSD growth of nano particle depend on the chemical purity, metal stoichiometric relationship of the metal ions, the solution stability and properties of the solutions.

Control of the nucleation and growth conditions will closely determine the final microstructure and functionality of the films. Different types of heating procedures have been used to prepare ferromagnetic, ferroelectric, multiferroic, metallic, semiconducting or superconducting materials.

11.9 Electrochemical deposition

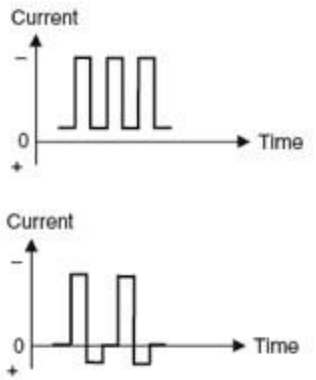
Electrochemical deposition is a deposition process in which metal ions in a solution are transported by an electric field to coat the surface of

a substrate. The deposition process can be cathodic or anodic reaction in nature. Electrodeposition of nanostructures can be obtained by controlling the electrolysis parameters. The most commonly practiced techniques are

- pulse current deposition to manipulate the growth of deposits,
- deployment of additives and surfactants to alter the grain size of deposits
- nanoparticles inclusion into deposits to form nanocomposites.

Electrochemical synthetic method can be used to synthesize silver nanoparticles (NPs). It is possible to control particle size by adjusting electrolysis parameters and to improve homogeneity of silver NPs by changing the composition of electrolytic solutions. Polyphenylpyrrole coated silver nanospheroids (3-20 nm) were synthesized by electrochemical reduction at the liquid/liquid interface. This nano-compound was prepared by transferring the silver metal ion from aqueous phase to organic phase, where it reacted with pyrrole monomer. In another study, monodisperse silver nanospheroids (1-18 nm) were synthesized by electrochemical reduction inside or outside zeolite crystals according to silver exchange degree of compact zeolite film modified electrodes. Furthermore, spherical silver NPs (10-20 nm) with narrow size distributions were conveniently synthesized in aqueous solution by an electrochemical method. Poly N-vinylpyrrolidone was chosen as the stabilizer for the silver clusters in this study. Poly N-vinylpyrrolidone protects NPs from agglomeration, significantly reduces silver deposition rate, and promotes silver nucleation and silver particle formation rate. Application of rotating platinum cathode effectively solves the technological difficulty of rapidly transferring metallic NPs from cathode vicinity to bulk solution, avoiding the occurrence of flocculates in vicinity of cathode, and ensures monodispersity of particles. Addition of sodium dodecyl benzene sulfonate to the electrolyte improved particle size and particle size distribution of silver NPs.

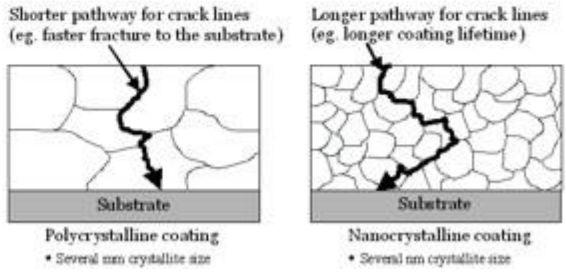
11.9.1 Pulse current electrodeposition of nanostructured coating



Pulsating the currents are used to achieve nanostructure coatings. The pulse parameters are pulse duty, pulse cycle, frequency, amplitude, cathodic and anodic current, zero current at open-circuit. Pulsating the deposition current can affects the diffusion layer next to the electrode surface which is in contact with the liquid solution. This will influence the deposition mechanisms of metal deposits such as altering the nucleation process and the subsequent growth of the deposit. Pulsed current can enable the incorporation of nanoparticles to a high content in the coating as well as producing a wider range of alloys, deposit composition and material properties

11.9.2 Deployment of electrolyte additives and surfactant technology

Electrolyte additives and surfactant technology are keys to the development of nanostructured materials and coatings. Surfactants can be categorised into groups such as: cationic, anionic, non-ionic or amphoteric. Surfactants can be hydrocarbon or fluorocarbon based. In the surface metal finishing industry, electrolyte additives are commonly grouped by names such as brighteners (provide surface finish as matte, semi-matte or bright appearance), surface wetters (reduce surface tension between, reduce coating porosity or liberation of gas bubbles) and stress relievers (relieve compressive or tensile stress of the coating). Additives and surfactants are deployed to affect the growth of metal deposits, via adsorption or desorption mechanisms.

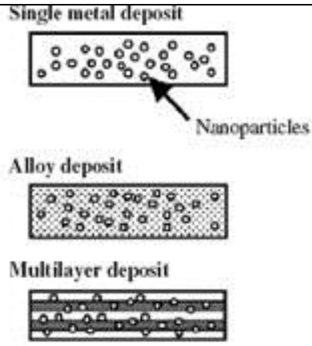


Many metallic coatings are conventionally designed on the macro-scale. By reducing the macro-scale to the nano-scale could provide enhanced surface properties, leading to a longer lasting, lighter

NOTE

weight and more protective coatings. Electrolyte additives and surfactants are used to affect the grain size of coating. The figure shows a polycrystalline *vs.* nanocrystalline coating. A nanocrystalline coating has nm grain size, with enhanced coating performance against an external load.

11.9.3 Nanoparticles in a metal coating to form nanocomposites



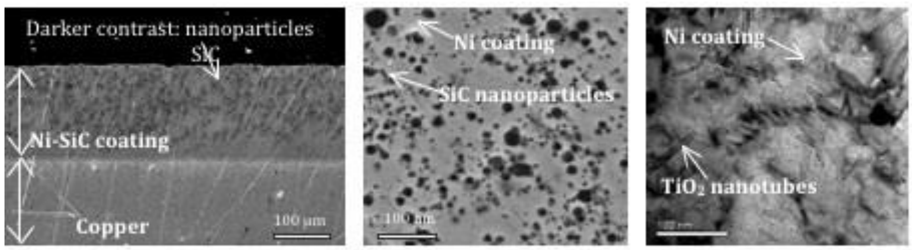
Nanosized particles can be incorporated into metallic coating to form nanocomposite coating. Two common processes involved in the incorporation of particles into metallic coatings are

(a) physical dispersion of particles in the electrolyte

(b) electrophoresis migration of particles to the work piece supported by surface

charged particles.

the inclusion of nanoparticles into a metal coating is dependent on many electrolysis parameters such as characteristics of the nanoparticle (particle concentration, surface charge, type, shape, size), electrolyte composition (electrolyte concentration, additives, temperature, pH, surfactant type and concentration), current density (direct current, pulsed current, potentiostatic control) and flow hydrodynamics (laminar, turbulent regimes), electrode geometry and electrodeposition reactor, eg. rotating disk electrode, rotating cylinder electrode, parallel plate electrodes, etc. Figures below show electrodeposited nickel coatings containing nanoparticles of silicon carbide (SiC) and titanium dioxide nanotubes (TiO_2), for wear and corrosion resistance. The metal coating can be plain metal, eg. nickel, copper, tin, gold, or alloys and multilayered coatings. Nanoparticles may include metals, alloys, ceramics, metal oxides, nitrides, carbides, etc.



11.10 Spray Pyrolysis Deposition

Spray pyrolysis is cost effective and can be easily performed in liquid phase. Substrates with complex geometries can be coated. Spray pyrolysis deposition leads to relatively uniform and high quality coatings. No high temperatures are required during processing up to 500^oC. Films deposited by spray pyrolysis are reproducible, giving it potential for mass production.The major interest in spray pyrolysis is due to its low cost, while it is increasingly being used for some commercial processes, such as the deposition of a transparent layer on glass , the deposition of a SnO_2 layer for gas sensor applications , the deposition of a stacked layer for solar cell applications , anodes for lithium-ion batteries , and optoelectronic devices .The general simplified scheme for spray pyrolysis deposition is shown in Fig. where three processing steps can be viewed and analyzed.

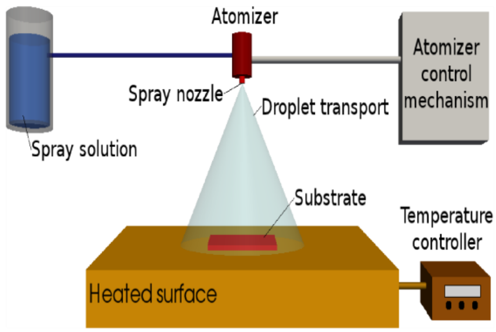


Fig. : General schematic of a spray pyrolysis deposition process.

The three processing steps for spray pyrolysis deposition are

1. Atomization of the precursor solution.
2. Aerosol transport of the droplet.
3. Droplet evaporation, spreading on the substrate, and drying and decomposition of the precursor salt to initiate film growth.

11.9 Check your progress questions

1. What is sputtering technique?
2. Explain the laser ablation mechanism of synthesizing nanoparticle
3. Write a note on CSD
4. How nano particles are prepared by electrodeposition method?
5. Discuss the spray pyrolysis method.

11.10 Answers to check your progress questions

1. Sputtering is a physical vapour deposition technique that has been used fabrication of nano particles. One of the biggest advantages of this

technique is that it allows the formation of highly pure and uniform thin films.

2. The mechanism of laser ablation depends on physical properties of metals and environment medium. Ablation of metal target commences with the sorption of laser beam energy. When the laser beam interacts with the metal target, the heat can generate and the photoionization of the metal target occurs. After that, metal nanoparticles will be released from the metal plate as the different phase that depends on the absorbed energy E and plasma plume expands.

3. CSD is a materials growth technique from precursor chemical solution of inorganic or organic metal salts dissolved in organic or water in stoichiometric ratios. The solutions are deposited on a substrate using spin coating, dip coating, web coating, ink jet printing, etc., depending on the requisites. The film thickness can be easily controlled by varying salts concentration based on the employed deposition technique. After the deposition, the solutions are dried and the chemical precursors are pyrolyzed to amorphous or nanocrystalline porous solid with well-defined thickness.

4. Electrochemical deposition is a deposition process in which metal ions in a solution are transported by an electric field to coat the surface of a substrate. The deposition process can be cathodic or anodic reaction in nature. Electrodeposition of nanostructures can be obtained by controlling the electrolysis parameters. The most commonly practiced techniques are

5. Spray pyrolysis is cost effective and can be easily performed in liquid phase. Substrates with complex geometries can be coated. Spray pyrolysis deposition leads to relatively uniform and high quality coatings. No high temperatures are required during processing up to 500^{o}C. Films deposited by spray pyrolysis are reproducible, giving it potential for mass production.

11.11 Summary

- Evaporation condensation and laser ablation are the important physical methods of preparing nanoparticles. The absence of solvent contamination and the uniformity distribution of nanoparticles (NPs) distribution in the prepared film are the advantages of physical synthesis over chemical processes.
- Vacuum evaporation is otherwise called as vacuum deposition and vaporization. In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum . The

vaporization source is the one that vaporizes materials by thermal processes.

- Sputtering is a physical vapour deposition technique that has been used fabrication of nano particles. One of the biggest advantages of this technique is that it allows the formation of highly pure and uniform thin films, and it has been developed for sputtering both metal (DC sputtering) and semiconductors (RF sputtering)..
- The mechanism of laser ablation depends on physical properties of metals and environment medium. Ablation of metal target commences with the sorption of laser beam energy. When the laser beam interacts with the metal target, the heat can generate and the photoionization of the metal target occurs.
- Electrochemical deposition is a deposition process in which metal ions in a solution are transported by an electric field to coat the surface of a substrate. The deposition process can be cathodic or anodic reaction in nature. Electrodeposition of nanostructures can be obtained by controlling the electrolysis parameters.

11.12 Keywords

Electrochemical deposition: It is a deposition process in which metal ions in a solution are transported by an electric field to coat the surface of a substrate.

Chemical vapour deposition (CVD): CVD is a chemical process used to produce high-purity, high-performance solid materials.

Sputtering: Quite versatile technique for the synthesis of nanoclusters and nanoparticles as it allows the usage of a quite broad range of materials as sputtering target.

Vacuum evaporation: In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum.

11.13 Self assessment question and exercise

1. What is spray deposition technique?
2. Explain in about pulsed laser deposition.
3. Wtite a note on vacuum evaporation process.
4. Give the advantages of CSD method.

11.14 Further Reading

1. C.N.R. Rao, A. Muller, A.K. Cheetam (Eds), The Chemistry of Nanomaterials, Vol.1, 2, Wiley – VCH, Weinheim, 2004.

2. C.P. Poole, Jr: F.J. Owens, Introduction to Nanotechnology Wiley Interscience, New Jersey, 2003

3. Kenneth J. Klabunde (Ed), Nanoscale materials in Chemistry, Wiley-Interscience, New York, 2001

UNIT- 12 Physical Characterization Techniques of Nanomaterial

Structure

Structure

12.0 Introduction

Nano science and technology is dynamic field that encompasses science and technologt. With rapid advances in areas such as molecular electronics, synthetic bio molecular motors, DNA-based self-assembly, and manipulation of individual atoms via a scanning tunnelling microscope, nanotechnology has become the principal focus of a growing cadre of scientists and engineers and has captured the attention and imagination of the general public. The fundamental nanotechnology lies in the fact that properties of material change drametically when their size is reduced to the nanometer range, but measuring this nano dimension is not a very easy task. Hence nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano charcterization techniques to allow a better control of morphology, size and dimensions of materials in nano range.

12.1 Objectives

After going through this unit you are able to

- Gain knowledge about various characterization techniques

- Understand surface properties of nanomaterial
- Acquire information about the surface analytical tools.

12.2 Fourier Transform – Infra Red Spectroscopy – FT-IR

A molecule may absorb IR radiation if it possesses change in dipole moment and its oscillating frequency is the same as the frequency of incident IR light. The absorption of IR radiation transfers energy to the molecule, inducing a corresponding covalent bond stretching, bending or twisting, which, in the case of a normal mode, is described by a stationary state of molecular vibrational Hamiltonian. Molecules without dipole moments such as N_2 and O_2, do not absorb IR radiation. Generally in a molecule, the vibrations involve various coupled pairs of atoms or covalent bonds, each of which must be considered as a combination of the normal modes; therefore the IR spectrum illustrating absorption or transmission versus incident IR frequency, can offer a fingerprint of the structure of the molecule of interest.

For nanomaterial applications, Fourier transform infrared (FTIR) spectroscopy is commonly employed to use the expression of characteristic spectral bands to reveal nanomaterial biomolecule conjugation. For *e.g.* proteins bound to nano particle surfaces, and to illustrate the conformational states of the bound proteins Furthermore, FTIR has also been extended to study nano-scaled materials, such as confirmation of functional molecules covalently grafted onto carbon nanotubes. A recently developed technique called attenuated total reflection (ATR)–FTIR spectroscopy uses the property of total internal reflection in conjunction with IR spectroscopy to probe the structure of adsorbed/deposited species at a solid/air or solid/liquid interface. In an ATR–FTIR system, the total internal reflectance, occurring within the equipped internal reflection element (IRE) crystal, which has a high refractive index at certain angles, forms evanescent waves that extend from the IRE crystal–sample interface into the sample with penetration depth of micrometers (0.5–5 µm), and the intensity of the evanescent waves decays exponentially from the interface. ATR–FTIR can provide IR absorption spectra to investigate, changes in surface properties as well as identification of chemical properties on the polymer surface when sample on the IRE–sample interface absorbs the evanescent IR waves with frequencies matching the vibrational modes of the sample. Although ATR–FTIR spectroscopy can be implemented to study the surface features of nanomaterials, it is not a very sensitive surface-analysis method at nanometer scale because the penetration depth of ATR–FTIR has the same order of magnitude as the incident IR wavelength.

12.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photo electron spectroscopy (XPS) and Auger electronic spectra (AES) involve the detection of electrons emitted from analyzed samples with kinetic energies less than2000 eV. Both the techniques are surface sensitive in nature and the wealth of information at shorter distances can be obtained from these technique without undergoing inelastic scattering and energy loss. The electrons detected in AES or XPS peaks are from the outer few nanometers of the material and notable structural information are obtained successfully. Catalysis is the area in which the technique has been applied and information regarding the enrichment or depletion of element on surface areas is obtained.Consequently, these two methods can be used with multiple approaches to obtain important information about layering or coatings nanoparticle on surfaces. X-ray and electron excitations produce Auger electrons incident electrons typically range in energy from 2 to 20 keV. X-rays (often Mg or Al Kα) are the incident radiation in XPS. This technique is also referred to as electron spectroscopy for chemical analysis (ESCA) by Nobel awardee Kai Siegbahn.

An electron beam can be focused to less than 10 nm in size, it is possible to analyze individual nanoparticles with AES. XPS aids to analyze collections of particles in a single layer or, in powder form and to obtain useful information. Both AES and XPS can be extremely important tools for determining the presence, composition, and thickness of coatings on nanoparticles, and surface enrichment and depletion at particle surfaces. XPS can also be used to determine particle sizes when conditions are not appropriate for analysis by other methods. The size, shape, and layered structure of nanoparticles influence XPS data in several different

ways including

Peak intensities and relative peak intensities of

- peaks for different elements
- different peaks for the same element
- the same peaks excited with different X-ray energies

Peak energies

- binding energies of peaks
- value of the Auger parameter
- Background signals from electrons that have lost energy

Although electron spectroscopies may not be as used in every situation where they would be appropriate, they are increasingly employed for nanoparticle characterization in a variety of ways. It is valuable to identify specific analysis objectives based on the type of research involved. Understanding the analysis objectives assists both the data collection and the nature of

the data processing. This can significantly improve the quality and value of the resulting information about the following are achieved easily

1. contamination, particle coatings, and oxidation
2. particle size
3. particle location
4. surface acidity and
5. electrical properties of particles

12.4 Laser Raman Spectroscopy

Raman scattering (RS) is a widely-used tool for structural characterization of nanomaterials and nanostructures that provides submicron spatial resolution for light-transparent material without the requirement of sample preparation, making it suitable for *in situ* experiments. The principle of RS is to measure the inelastic scattering of photons possessing different frequencies from the incident light after interacting with electric dipoles of the molecule. The process of RS results in frequency differences between the incident photons and the inelastically scattered photons associated with the characteristics of the molecular vibrational states, during which the inelastically scattered photons emitting frequencies lower than the incident photons refer to the Stokes lines in Raman spectrum and the inelastically scattered photons emitting frequencies higher than the incident photons are named Anti-Stokes lines. RS is generally considered to be complementary to IR spectroscopy, *i.e.*, vibrational modes that are Raman active should be IR inactive, and vice versa, for small symmetrical molecules, because Raman transitions result from nuclear motion modulating the polarizability of the molecules, rather than a net change in the dipole moment of the molecules.

One of the major advantages of RS is that it is suitable for studying biological samples in aqueous solution because water molecules tend to be weak Raman scatterers. Furthermore, the detailed molecular information offered by RS can be used to investigate conformations and concentrations of tissue constituents, which demonstrates the potential of RS for detecting tissue abnormalities. However, while the conventional RS technique provides indirect characterization of nanomaterials, such as average size and size distribution through analysis of the spectral line broadening and shift, it lacks the spatial resolution necessary to delineate different domains for application in nanotechnology. Other downsides of conventional RS include interference of fluorescence and extremely small cross section, demanding intense laser excitation and a large amount of sample materials to provide sufficient RS signals. In contrast, implementation of surface enhanced Raman scattering (SERS) can strongly enhance RS signals and increase spatial resolution while the measured biomolecules are adhered to the surface of metallic structures, such as commonly used gold or silver NP colloid substrates. SERS can be used to (i) study surface functionalization of metallic NPs, (ii) monitor the conformational change in proteins conjugated to the metallic NPs,

and (iii) track intracellular drug release from the nanoplatform and measurement of the pH in the surrounding medium. By adapting the concept of confining the light field in Raman near-field scanning optical microscopy to overcome diffraction-limited resolution, a recently emerging technique, tip-enhanced Raman spectroscopy (TERS), utilizes an apertureless metallic tip instead of an optical fiber to gain the surface enhancement of the Raman signals (the SERS effect). In contrast to conventional RS, SERS and TERS provide topological information of the nanomaterials, in addition to their structural, chemical and electronic properties, which conventional RS provides. However, the lack of measurement reproducibility in SERS caused by the size and shape variation, as well as undesirable aggregation of NPs is an obstacle for *in vitro* or *in vivo* imaging applications.

12.5 X-ray diffraction (XRD) analysis

In a variety of X-ray spectroscopic modalities, XRD is a primary tool for completely resolving the tertiary structures of crystalline materials at the atomic scale. The diffraction of X-ray can be simply described as the reflection of a collimated beam of X-rays incident on the crystalline planes of an examined specimen according to Bragg's law. Typically, XRD, based on wide-angle elastic scattering of X-rays, is a tool for characterizing crystalline size, shape and lattice distortion by long-range order, but is limited to disordered materials. Although XRD is a well-established technique and has frequently been used to determine the material structure at the atomic scale, difficulty in growing crystals and the ability of getting results only from single conformation/binding state of the sample limit the applications of XRD technique. Another disadvantage of XRD is the low intensity of diffracted X-rays, particularly for low atomic number materials, compared with electron diffraction. A recent X-ray diffraction study reported a new approach using femtosecond pulses from a hard-X-ray free-electron laser for structure determination, which may benefit structure determination of macromolecules.

12.6 Microscopic techniques

The following microscopic techniques are usually employed for the characterization of nanoparticles.

12.7 Scanning electron microscopy (SEM)

In contrast to optical microscopy, which uses light sources and glass lenses to illuminate specimens to produce magnified images, electron microscopy (EM) uses beams of accelerated electrons and electrostatic or electromagnetic lenses to generate images of much higher resolution, based on the much shorter wavelengths of electrons than visible light

photons. SEM is a surface imaging method in which the incident electron beam scans across the sample surface and interacts with the sample to generate signals reflecting the atomic composition and topographic detail of the specimen surface. The incident electrons cause emissions of elastic scattering of electrons, referring to backscattered electrons, inelastic scattering of electrons named low-energy secondary electrons, and characteristic X-ray light called cathodoluminescence from the atoms on the sample surface or near-surface material. Among these emissions, detection of the secondary electrons is the most common mode in SEM and can achieve resolution smaller than 1 nm.

The size, size distribution and shape of nanomaterials can be directly acquired from SEM; however, the process of drying and contrasting samples may cause shrinkage of the specimen and alter the characteristics of the nanomaterials. In addition, while scanned by an electron beam, many biomolecule samples that are nonconductive specimens tend to acquire charge and insufficiently deflect the electron beam, leading to imaging faults or artifacts. Coating an ultrathin layer of electrically conducting material onto the biomolecules is often required for this sample preparation procedure. Because a cryogenic freezing method is often required in EM to image surface groups attached to NPs, the size of nanomaterial cannot be investigated in physiological conditions. An exception is environmental SEM (ESEM), through which samples can be imaged in their natural state without modification or preparation. Because the sample chamber of ESEM is operated in a low-pressure gaseous environment of 10–50 Torr and high humidity, the charging artifacts can be eliminated, and coating samples with a conductive material is no longer necessary Still, most of the EM techniques, including SEM, possess the disadvantage of a destructive sample preparation, prohibiting its analysis by other modalities. In addition, biased statistics of size-distribution of heterogeneous samples is unavoidable in SEM due to the small number of sample particles in the scanning region.

12.8 Atomic force microscopy (AFM)

Unlike STM, AFM does not require oxide-free, electrically conductive surfaces for nano measurement and this scanning probe imaging tool consisting of a micro-machined cantilever with a sharp tip at one end to detect the deflection of the cantilever tip caused by electrostatic and van der Waals repulsion, as well as attraction between atoms at the tip and on the measured surface. The oscillating cantilever then scans over the surface of specimen to generate an image with a vertical resolution of around 0.5 nm. Like SEM and TEM techniques, AFM can be used for investigating the size, shape, structure, sorption, dispersion and aggregation of nanomaterials. The different scanning modes employed in AFM studies include noncontact mode (also called static mode), contact

mode and intermittent sample contact mode (also called dynamic mode and tapping mode). In addition to probing the sizes and shapes of nanomaterials under physiological conditions, AFM is capable of characterizing dynamics between nanomaterials in biological situations, such as observing the interaction of nanomaterials with supported lipid bilayers in real time, which is not achievable with current EM techniques. AFM is gaining importance due to its capability for imaging biomaterials without causing appreciable damage to many types of native surfaces. The main strength of AFM is its capability to image a variety of biomaterials at the sub-nanometer scale in aqueous fluids. However, a major drawback is that the size of the cantilever tip is generally larger than the dimensions of the nanomaterials examined, leading to unfavorable overestimation of the lateral dimensions of the samples. Unlike fluorescence techniques, AFM lacks the capability of detecting or locating specific molecules; however, this disadvantage has been eliminated by recent progress in single-molecule force spectroscopy with an AFM cantilever tip carrying a ligand, a cell adhesion molecule or chemical groups, which can probe or detect single functional molecules on cell surfaces.

12.9 Transmission electron microscopy (TEM)

As the most frequently used technique for characterizing nanomaterials in EM, TEM provides direct images and chemical information of nanomaterials at a spatial resolution down to the level of atomic dimensions (<1 nm). In the conventional TEM mode, an incident electron beam is transmitted through a very thin foil specimen, during which the incident electrons interacting with specimen are transformed to unscattered electrons, elastically scattered electrons or inelastically scattered electrons. The magnification of TEM is mainly determined by the ratio of the distance between objective lens and the specimen and the distance between objective lens and its image plane. The scattered or unscattered electrons are focused by a series of electromagnetic lenses and then projected on a screen to generate an electron diffraction, amplitude-contrast image, a phase-contrast image or a shadow image of varying darkness according to the density of unscattered electrons.In addition to the high spatial resolution of TEM that enhances the morphological and structural analyses of nanomaterials, a wide variety of analytical techniques can be coupled with TEM for different applications; for example, chemical analyses of electron energy loss spectroscopy and energy dispersive X-ray spectroscopy can quantitatively investigate the electronic structure and chemical composition of the nanomaterials, respectively.

Overall, both TEM and SEM can reveal the size and shape heterogeneity of nanomaterials, as well as the degrees of aggregation and dispersion. TEM has advantages over SEM in providing better spatial resolution and

capability for additional analytical measurements. There are certain drawbacks accompanying the advantages of TEM. A significant tradeoff is that a high vacuum and thin sample section are required for electron-beam penetration in TEM measurement. Sample destruction and measurement in unnatural/non-physiological conditions are common to all EM techniques. In general, high-resolution EM imaging enables examination of a minute part of the specimen over a certain period of time and results in poor statistical sampling. Also, abundant artifacts are generated due to 3D specimens being probed by the 2D TEM technique in transmission view, leading to no depth sensitivity for a single TEM image. Another limitation is that specimens have to be thin enough to transmit sufficient electrons to produce images; in particular cases, the specimen thickness of less than 50 nm is required while doing high-resolution TEM or electron spectroscopy. The extensive preparation of thin specimens increases the possibility of altering sample's structure and makes TEM analysis a very time consuming process. Another big concern is that TEM specimens can be damaged or even destroyed by intense, high-voltage electron beams.

Interestingly, wet TEM can be used for determining the particle size, dispersion, aggregation/agglomeration and dynamic displacement of nanomaterials in an aqueous environment. In addition to adapting the function of ESEM for observing samples under partial water vapor pressure in the microscope specimen chamber, a recently developed wet scanning transmission electron microscopy (STEM) imaging system enables transmission observation of species totally submerged in a liquid phase, compared with the issues of poor contrast and possible drifting of objects occurring in the images of the top surface of the liquid using ESEM. Thus, the wet mode STEM permits observation in nanoscale resolution and high contrast even through several micrometers of water, without adding contrast agents and stains.

12.10 Thermal analysis: TGA/DTA and DSC

The thermal stability and the amount of the nanomaterial conjugates can be evaluated using several thermal techniques. The temperature-dependent weight change in bulk samples, such as various nanomaterial bioconjugates, can be monitored using thermal gravimetric analysis TGA and DTA. Material transitions such as melting, crystallization, glass transition and decomposition of nanomaterial-bioconjugates can be accessed through differential scanning calorimetry (DSC); therefore, subsequent analysis of DSC measurements can provide the structure and stability of the investigated material. In addition, the stoichiometry, affinity and enthalpy derived from the interaction between nanomaterial and biomolecule can be determined using isothermal titration calorimetry (ITC). The thermal stability and the amount of the nanomaterial conjugates can be evaluated using several thermal

techniques. The temperature-dependent weight change in bulk samples, such as various nanomaterial bioconjugates, can be monitored using thermal gravimetric analysis TGA and DTA. Material transitions such as melting, crystallization, glass transition and decomposition of nanomaterial-bioconjugates can be accessed through differential scanning calorimetry (DSC); therefore, subsequent analysis of DSC measurements can provide the structure and stability of the investigated material. In addition, the stoichiometry, affinity and enthalpy derived from the interaction between nanomaterial and biomolecule can be determined using isothermal titration calorimetry (ITC). By locally heating the sample to generate a temperature gradient, thermophoresis monitors the motion of the sample to evaluate its size and surface potential. However, thermophoresis needs higher concentrations of the examined species than FCS does to ensure robust signals.

12.11 Check Your Progress Questions

1. What sort of information is obtained from FT-IR spectra of nano particles?
2. Write note on characterization of nano particles by Raman spectra.
3. Explain the wealth of information obtained from nano particles using XRD.
4. What is the minimum level osf surface scanned by AFM?

12.12 Answers to check your progress questions

1. Fourier transform infrared (FTIR) spectroscopy is commonly employed to use the expression of characteristic spectral bands to reveal nanomaterial biomolecule conjugation.

2. Raman scattering (RS) is a widely-used tool for structural characterization of nanomaterials and nanostructures that provides submicron spatial resolution for light-transparent material without the requirement of sample preparation, making it suitable for *in situ* experiments. The principle of RS is to measure the inelastic scattering of photons possessing different frequencies from the incident light after interacting with electric dipoles of the molecule.

3. In a variety of X-ray spectroscopic modalities, XRD is a primary tool for completely resolving the tertiary structures of crystalline materials at the atomic scale. The diffraction of X-ray can be simply described as the reflection of a collimated beam of X-rays incident on the crystalline planes of an examined specimen according to Bragg's law. Typically, XRD, based on wide-angle elastic scattering of X-rays, is a tool for

characterizing crystalline size, shape and lattice distortion by long-range order, but is limited to disordered materials.

4. The oscillating cantilever then scans over the surface of specimen to generate an image with a vertical resolution of around 0.5 nm.

12.13 Summary

- For nanomaterial applications, Fourier transform infrared (FTIR) spectroscopy is commonly employed to use the expression of characteristic spectral bands to reveal nanomaterial biomolecule conjugation.
- The size, size distribution and shape of nanomaterials can be directly acquired from SEM
- Both TEM and SEM can reveal the size and shape heterogeneity of nanomaterials, as well as the degrees of aggregation and dispersion
- The thermal stability and the amount of the nanomaterial conjugates can be evaluated using several thermal techniques. Such as TGA, DSC etc

12.14 Keywords

TEM: Transmission electron microscope provides direct images and chemical information of nanomaterials at a spatial resolution down to the level of atomic dimensions of <1 nm

Thermal techniques: The thermal stability and the amount of the nanomaterial conjugates can be evaluated using several thermal techniques

AFM: Atomic force microscope can be used for investigating the size, shape, structure, sorption, dispersion and aggregation of nanomaterials

XPS: X-ray photo electron spectroscopy for studying surface properties of nano materials

12.15 Self-assessment questions and exercises

1. What level of information is obtained for nano particles from laser Raman spectra?
2. Explain in detail about XPS for characterization of nano particles.
3. Give the importance of TEM in characterzing nano particle
4. Explain how thermal aids in structural analysis of nano materials.

12.16 Further readings

1. H. Fujita (Ed.), Micromachines as tools in nanotechnology, Springer-Verlag, Berlin, 2003.

2. H. Gleiter , Nanostructured Materials: Basic Concepts, Microstructure and Properties

3. C.N.R. Rao, A. Muller, A.K. Cheetam (Eds), The Chemistry of Nanomaterials, Vol.1, 2, Wiley – VCH, Weinheim, 2004.

4. C.P. Poole, Jr: F.J. Owens, Introduction to Nanotechnology Wiley Interscience, New Jersey, 2003

5. Kenneth J. Klabunde (Ed), Nanoscale materials in Chemistry, Wiley-Interscience, New York, 2001

Unit-13: Computer Application in Chemistry

Structure

13.0 Introduction

Computer plays a very important role in every aspect of our lives, including chemistry. The fields of applications of computer is chemistry are

a) Computational Chemistry
b) Chemometrics
c) Chemoinformatics.

A branch of chemistry that uses the results of theoretical chemistry incorporated into efficient computer programs to calculate the structures and properties of molecules and solids, applying these programs to real chemical problems. Computational chemistry when a mathematical method is well developed and can be implemented on a computer such as quantum mechanics, molecular mechanics, simulation, minimization, conformational analysis.

13.1 Objective

The students must be able to use the computer to solve problems in Chemistry, specifically they have to efficiently use:

a. spreadsheets;
b. software for solving algebraical problems
c. software for solving numerical problems;
d. software for the representation of molecular structures.

13.2 Calculation of pH

Illustration

pH of a solution if the $[H^{1+}]$ is $1*10^{-5}$ M

pH= - $\log[H^+]$

pH= - $\log[1*10^{-5}]$

pH=5

Program

```
10 PRINT "ENTER PH VALUE"
20 INPUT num
30 LET P= - LOG(num)
40 PRINT "THE VALUE OF PH FOR THE GIVEN VALUE IS"
50 PRINT P
60 END
```

13.3 Solubility Product

Illustration

The equilibrium constant expression for this dissolution is called a solubility product constant.

K_{sp} = solubility product constant

K_{sp} = [Ag+[][cl-]=$1.8*10^{-10}$

Molar concentration of ions raised to their stoichiometric powers at equilibrium

Program

```
10 PRINT "ENTER THE CONCENTRATIONS OF IONS"
20 INPUT Ag,Cl
30 LET Ksp=Ag *Cl
40 PRINT " THE SOLUBILITY PRODUCT VALUES ARE"
50 PRINT Ksp
60 END
```

13.4 Calculation of Bond Energy Using Born-Lande Equation

Illustration

$$E = -\frac{N_A M z^+ z^- e^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

where:

- N_A = Avogadro constant;

NOTE

- *M* = Madelung constant, relating to the geometry of the crystal;
- z^+ = numeric charge number of cation
- z^- = numeric charge number of anion
- *e* = elementary charge, 1.6022×10^{-19} C
- ε_0 = permittivity of free space
  $4\pi\varepsilon_0 = 1.112\times10^{-10}$ $C^2/(J\cdot m)$
- r_0 = distance to closest ion
- *n* = Born exponent, typically a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically.[3]

Program

```
10 PRINT " BORN- LANDE EQUATION"
20 DIM E,N,M,Z1,Z2, e1,e2 ,R,n
30 INPUT "ENTER AVOGADRO CONSTANT " , N
40 INPUT "ENTER MADELUNG CONSTANT" , M
50 INPUT "ENTER NUMERIC CHARGE NUMBER OF
CATION" , Z1
60 INPUT "ENTER NUMERIC CHARGE NUMBER OF
ANION" , Z2
70 INPUT "ENTER ELEMENTARY CHARGE" , e1
80 INPUT "ENTER PERMITTIVITY OF FREE SPACE" , e2
90 INPUT "ENTER DISTANCE TO CLOSEST ION " , R
100 INPUT "ENTER BORN EXPONENT" , n
110  LET  E= -(N*M*Z1*Z2* e1* e1)/(4*3.17*e2*R)*(1-(1/n))
120 PRINT "BORN LANDE EQUATION VALUE IS"
130 PRINT E
140 END
```

13.5 Standard Deviation and Correlation Coefficient

Illustration

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \overline{x})^2}$$

For calculating standard deviation

1. Calculate the average
2. Calculate the deviation,score minus the average
3. Square the deviation
4. Sum up the squared deviations

5. Divide this by the number of scores in your data set
6. Take the square root.

Program

```
10 PRINT "BASIC PROGRAM TO CALCULATE STANDARD DEVIATION  OF TWO NUMBERS"
20 DIM N,I as integer
30 DIM MEAN,  VARIANCE, SD, SUM, DIFFER, VARSUM  AS INTEGER
40 DIM P [50] AS INTEGER
50 LET SUM=0, VARSUM=0
60 PRINT "PLEASE ENTER THE N VALUE"
70 INPUT N
80 PRINT "ENTER THE VALUES"
90 FOR I=1 TO N
90 INPUT P [I]
100 SUM=SUM + P [I]
110 NEXT I
120 MEAN=SUM/N
130 FOR I=1 TO N
140 DIFFER=P [I]-MEAN
150 VARSUM=VARSUM+ POW (DIFFER,2)
160 NEXT I
170 VARIANCE=VARSUM/N
180 SD=SQRT (VARIANCE)
190 PRINT "THE MEAN VALUE IS", MEAN
200 PRINT "THE VARIANCE VALUE IS", VARIANCE
210 PRINT "STANDARD DEVIATION IS ", SD
220  END
```

Correlation coefficient

Illustration

NOTE

Formula

$$r = \frac{Cov(X, Y)}{\sigma_x \, \sigma_y}$$

$$r = \frac{\sum XY}{n \, \sigma_x \, \sigma_y}$$

$$r = \frac{\sum XY}{\sqrt{\sum X^2 \sum Y^2}}$$

where
$X = x - \bar{x}$
$Y = y - \bar{y}$

r → Correlation Coefficient
σ_x → standard deviation of dataset X
σ_y → standard deviation of dataset Y
$\bar{x}$ → mean of dataset X
$\bar{y}$ → mean of dataset Y
n → number of data points

Program

```
10  PRINT "PROGRAM TO FIND CORRELATION
COEFFICIENT"
 20  DIM  x[100], y[100], xy[100], xsquare[100], ysquare[100] AS
INTEGER;
 30  DIM  i, n, xsum, ysum, xysum, xsqr_sum, ysqr_sum AS
INTEGER
 40  DIM  coeff, num, deno AS LONG
 50   LET  xsum = ysum = xysum = xsqr_sum = ysqr_sum = 0;
 60   REM  get the number of entries from the user
 70   PRINT "Enter the value for n:"
 80   INPUT n
 90   REM  get the values for x and y  from the user
 100  PRINT "Enter the value for x and y:"
 110  FOR i=O TO  0; i < n;
 120 PRINT "x[i] , y[i]: "
 130  PRINT x[i], y[i]
 140  REM  find the needed data to manipulate correlation coeff
 150  FOR i=0 to n
 160  xy[i] = x[i] * y[i];
 170  xsquare[i] = x[i] * x[i];
 180  ysquare[i] = y[i] * y[i];
 190  xsum = xsum + x[i];
```

```
200  ysum = ysum + y[i];
210  xysum = xysum + xy[i];
220  xsqr_sum = xsqr_sum + xsquare[i]
 230  ysqr_sum = ysqr_sum + ysquare[i];
 240   num = 1.0 * ((n * xysum) - (xsum * ysum));
 250  deno = 1.0 * ((n * xsqr_sum - xsum * xsum)* (n * ysqr_sum -
ysum * ysum));
 260 REM  calculate correlation coefficient
 270 coeff = num / sqrt(deno);
 280 REM  print the result
 290 PRINT "Correlation Coefficient : "
 300 PRINT  coeff
 310 END
```

13.4 Check your progress question

1. What is called solubility product constant for Silver Chloride?
2. Give the formula for Born-Lande equation
3. What is the formula to calculate Standard Deviation and Correlation Coefficient

13.5 Answers to check your progress questions

1. The equilibrium constant expression for this dissolution is called a solubility product constant

Ksp=solubility product constant

Ksp=[Ag+[][cl-]=1.8*10 $^{-10}$

2.

$$E = -\frac{N_A M z^+ z^- e^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

3.

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \overline{x})^2}$$

NOTE

13.6 Keywords

Solubility Product Constants: The equilibrium constant expression for this dissolution is called a solubility product constant
Madelung constant : Relating to the geometry of the crystal.
Standard deviation: It is a measure of the dispersion of data from its average. Covariance is a measure of how two variables change together, but its magnitude is unbounded, so it is difficult to interpret
Correlation : Correlation is a statistical measure that indicates the extent to which two or more variables fluctuate together.

13.7 Summary

- pH is an important quantity that reflects the chemical conditions of a solution. The pH can control the availability of nutrients, biological functions, microbial activity, and the behavior of chemicals.
- The standard deviation is the best measure of variation. It is based on every item of the distribution. You can do algebraic operation and is less affected by fluctuations of sampling than most other measures of dispersion.
- The Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion
- A solubility product, or K_{sp}, is the equilibrium constant for a chemical reaction in which a solid ionic compound dissolves to yield its ions in solution.

13.8 Self-assessment questions and exercises

1. What is called solubility product constant for Silver Iodide?
2. Calculate the pH value for 0.05m sodium hydroxide solution.
3. Gabriella asked 555 of her hundreds of coworkers how much storage space they were currently using on their computer. Here are their responses (in gigabytes): 4, 8, 8, 9, 114,8,8,9,11. Calculate standard deviation.

13.9 Further Reading

1. BASIC Programming for Chemists, P.C.jurns, T.L.Isenhour and C.C.Wilkins, JWS & Sons ,1987

2. Computers in Chemistry, K.V.Raman, Tata McGraw Hill, New Delhi,1993.

UNIT-14: Online Resources for Chemistry

Structure

14.0 Introduction

Chemistry Education serves the dual purpose of preparing those conducting research in academia or chemical-based industry production, as well as those teaching chemistry as general education. The boundaries between chemistry and other subjects such as biology, physics and environmental science, are blurring. Contemporary chemistry education has expanded beyond a general understanding of the nature of chemistry to include problem solving, scientific inquiry and other technical skills required in the modern scientific community. Topics in research and teaching, including team-based learning, chemical data visualization, instruction technologies and laboratory learning, merge developments in both natural science and educational practices.

14.1 Objective

After going through this unit you are able to

- Understand the various online resources available on net
- Know about the various journal for publishing chemistry research work
- Acquire knowledge about search engines

- Gain the importance of accessing net for studying chemistry

14. 2 Internet Service Providers

This guide is focused on web resources serving instructors at the secondary level and above, chemistry education researchers, academic librarians, practicing chemists and chemical technologists. The purpose of this webliography is to collect some of the best resources on chemistry teaching and learning and educational research.Online resources, including web sites, databases, e-books, bibliographies, etc., were reviewed and evaluated to compile this webliography. The criteria for selection included relevancy, target audience, authority, accuracy, and currency. This webliography is not exhaustive, but includes the most relevant resources in chemistry education and related fields. All resources except subscription-based journals are free and publicly accessible. Major Web Sites list comprehensive teaching and learning resources for all levels of education.

Organizations consist of professional and other organizations that are either independent or nested in chemistry or education associations. Publications include both scientific magazines and academic journals. Academic journals publish articles on theoretical perspectives, laboratory practices, literature reviews, and experimental papers, including systematic evaluations of innovative practice. Conferences and Meetings include major national and international conferencesfor chemistry and chemistry education, where instructors and scholars gather annually or biannually to share experiences and communicate innovative ideas. Academic Programs and Research Centers list units supported by colleges and universities that serve education and research at the college level and above. Resources for Teaching Chemistry provide classroom teaching and laboratory resources for hands-on activities that include guidelines, safety issues, demonstrations and tutorials.

Notified Web Sites are,

Name of web site	**Link to the website**	**About the website**

Education, American Chemical Society (ACS)	http://www.acs.org/content/acs/en/education.html	provides comprehensive teaching and learning resources from elementary school to graduate school. It covers chemistry education in the broadest sense, including lab tutorials, online examinations, workshops and seminars, textbooks, news, reports, e-books, and scholarly publications.
ChemCollective	http://chemcollective.org/home	ChemCollective is a collection of engaging, online activities created by Carnegie Mellon University faculty who are interested in chemistry education. It provides virtual labs, scenario-based learning activities, tutorials and concept tests.
ChemistryGuide	http://www.chemistryguide.org/	This site provides a directory and search engine of chemistry resources. There are approximately 250 resources in the directory, and it can be browsed by topics such as green chemistry and chemistry dictionaries.
LearnChemistry	http://www.rsc.org/learn-chemistry/collections/Higher-Education/	Learn Chemistry Higher Education is published by the Royal Society of Chemistry and provides practical guides for students and instructors on how to read a scientific article, how to cite sources in the Royal Society of Chemistry format and how to perform pedagogical research in the STEM disciplines.
Chemical Education Digital Library (ChemEd DL)	http://www.chemeddl.org/	Sponsored by the National Science Foundation, ChemEd DL provides access to numerous digital, educational resources, such as an interactive Periodic Table, organic stereochemistry tutorials, a virtual laboratory, biographies of chemists and more.
The Green Chemistry Education Network (GCEdNet)	http://cmetim.ning.com/	Sponsored by the University of Oregon and the National Science Foundation, GCEdNet is a network of educators from colleges, universities, community colleges and high schools who exchange ideas on incorporating green chemistry into the curriculum. This site also includes links to green chemistry news resources published

NOTE

		by the American Chemical Society, Yale University, the University of Massachusetts Lowell and other organizations.

14.2.1 Resources for Chemistry Teaching

Name of website	Link to the website	About the website
ACS Examinations Institute	http://chemexams.chem.iastate.edu/	The ACS Examinations Institute produces standardized exams in various subdisciplines of chemistry. It offers instructors and students electronic delivery of exams, exam statistics and information about laboratory assessment and research projects
Process Oriented Guided Inquiry Learning (POGIL) Curriculum Materials	https://pogil.org/resources/curriculum-materials/classroom-activities	POGIL is a research-based, student-centered teaching methodology, which originated in chemistry classes in colleges in the 1990s. POGIL replaced lectures with guided inquiry through self-managed collaborative learning among students along a three-phase learning cycle: the "Exploration" phase, the "Concept Invention" or "Term Introduction" phase, and the "Application" phase (Moog & Spencer 2008). This teaching methodology enhances content mastery, problem-solving skills and lifelong learning. This site provides curriculum materials and resources for instructors to implement the POGIL teaching approach as facilitators at the high school level and above. The POGIL Project is sponsored by the National Science Foundation, the Department of Education and other foundations.
Chalkbored	http://www.chalkbored.com/index.htm	Chalkbored is a web-based book created by Jeremy Schneider for sharing practical education issues. Chalkbored Chemistry 11 and

		Chemistry 12 provide worksheets, handouts, labs and slides for high school chemistry teaching. All materials are free to download for classroom teaching or personal use.
Resources for Chemistry Education	http://www.chem1.com/chemed/	This site provides annotated web links to instructional materials for chemistry teachers in settings ranging from K-12 schools to the undergraduate level. Resources include open access textbooks, reviews, reference information, homework, quizzes and policy information.
Virtual Chemistry	http://www.chem.ox.ac.uk/vrchemistry/	Sponsored by Oxford University, Virtual Chemistry applies a three-dimensional simulated laboratory to chemistry instruction. The Virtual Experiments section of the web site provides interactive tutorials and quizzes. The site also features links to 3-D demonstrations, an interactive periodic table and 3-D reaction mechanisms.

14.3 Terms used in email

Attachment

An attachment is a file (such as an image, a word processing document or an mp3 file perhaps) that is sent along with an email message.

Backscatter

Backscatter is a delivery failure report generated by a junk email that used an innocent third party's email address as the sender (which address receives the delivery failure message).

Base64

Base64 is a method for encoding arbitrary binary data as ASCII text, to be used, for example, in an email body.

Bcc (Blind Carbon Copy)

A Bcc, short for "blind carbon copy", is a copy of an email message sent to a recipient whose email address does not appear (as a recipient) in the message.

Blacklist

A Blacklist collects known sources of spam. Email traffic can then be filtered against a blacklist to remove spam from these sources.

Cc

A Cc, short for "carbon copy", is a copy of an email message sent to a recipient whose email address appears in the message's Cc header field.

Email Address

An email address is a name for an electronic postbox that can receive (and send) email messages on a network (such as the internet or a local network not connected to the wider internet).

Email Body

The email body is the main part of an email message that contains the message’s text, images and other data (such as attached files).

Email Client

An email client is a program (on a computer or mobile device, for example) used to read and send electronic messages.

Email Header

Email header lines make up the first part of an email message. They contain information used to control the message and its transmission as well as meta-data such as the Subject, origin and destination email addresses, the path an email takes, and maybe its priority.

Email Server

An email server is a program running at Internet Service Providers and large sites used to transport mail. Users normally do not interact with email servers directly: email is submitted with an email client to an email server, which delivers it to the recipient's email client.

From

The "From:" header field, in an email, contains the message's author. It must list the email address, and one can add a name as well.

GB

A GB (gigabyte) is made up of 1000 MB (megabytes) or 10^9 (1 billion) bytes. A byte is a basic unit of storing information electronically made up of 8 bits; each bit has two states (on or off).

IMAP (Internet Messaging Access Protocol)

IMAP, short for Internet Messaging Access Protocol, is an internet standard that describes a protocol for retrieving mail from an email (IMAP) server. IMAP allows email programs to access not only new messages but also folders on the server. Actions are synchronized between multiple email programs connected through IMAP.

IMAP IDLE

IMAP IDLE is an optional expansion of the IMAP email accessing protocol that allows the server to send new message updates to the client in real time. Instead of having your email program check for new mail every few minutes, IMAP IDLE allows the server to notify your email program when new messages have arrived. You can see incoming mail immediately.

LDAP (Lightweight Directory Access Protocol)

LDAP, short for Lightweight Directory Access Protocol, defines a means to find and edit information in white pages. Using LDAP, email, groupware, contact and other software can access and manipulate entries on a directory server.

List-Unsubscribe

List-Unsubscribe is an optional email header line that lets mailing list administrators specify means to unsubscribe from a mailing list or newsletter. Email programs and web-based email services can use this header to offer an easy method for unsubscribing.

Mailto

Mailto is an HTML tag that allows visitors to a site to click on a link that creates a new message in their default email program. It is possible to set not only a default email recipient but also default Subject and message body content.

MIME (Multipurpose Internet Mail Extensions)

MIME, short for Multipurpose Internet Mail Extensions, specify a method to send content other than ASCII text via email. Arbitrary data is encoded as ASCII text for MIME.

Phishing

Phishing is a fraudulent practice in which private data is captured on websites or through an email designed to look like a trusted third

NOTE

party. Typically, phishing (from "password fishing") scams involve an email alerting the user to a problem with their bank or another account.

POP (Post Office Protocol)

POP (Post Office Protocol) is an internet standard that defines an email server and a way to retrieve mail from it. In contrast to IMAP, POP only lets the email client download recent messages, to be managed in the client and on the device.

PST (Personal Folders File)

PST, short for Personal Folders File, is the format used by Microsoft Outlook to store data locally. A PST file holds emails, contacts, notes, the to-do list, calendars, and other Outlook data.

Public Key Cryptography

Public key cryptography uses a key with two parts. The public key part is used for encryption exclusively for the recipient, whose private key part is applied for decryption. For public key cryptography to be safe it is important that only the intended recipient knows the private part of the key.

RFC (Request For Comments)

Request For Comments (RFC) is the format Internet standards are published in. RFCs relevant for email are published by the Internet Engineering Task Force (IETF) and include RFC 821 for SMTP, RFC 822, which specifies the format of Internet email messages, or RFC 1939, which lays down the PO protocol.

S/MIME

S/MIME is a standard for secure email messages. S/MIME messages offer sender authentication using digital signatures and can be encrypted to protect privacy.

SMTP (Simple Mail Transfer Protocol)

SMTP, short for Simple Mail Transfer Protocol, is the protocol used for outgoing email on the Internet. It defines a message format and a procedure to route messages through the Internet from source to destination via email servers.

Spam

Spam is unsolicited email. Not all unsolicited email is spam, however. Most spam is sent in bulk to a large number of email addresses and advertises some product or—considerably less often—political viewpoint.

Spammer

A spammer is a person or entity (such as a company) that sends spam emails

Spamvertise

Something is spamvertised when it is promoted (or merely appears) in spam. The term is commonly used with Web sites or email addresses that are part of the body of an unsolicited commercial email.

Subject

The "Subject" of an email message should be a short summary of its contents. Email programs usually display it in a mailbox display together with the sender.

Threadjacking

Threadjacking (also threadwhacking) is to steer off the original topic in an email thread, especially on a mailing list. Threadjacking can also apply to other conversations on the internet, of course, say on message boards, blogs or social networking sites. Whether the threadjacker changes the subject line to reflect the change in subject or retains the original email subject, to take over a thread can be regarded as threadjacking in either case.

To

The To: line of an email contains its primary recipient or recipients. All recipients in the To: line is visible to all other recipients, possibly by default.

Unicode

Unicode is a way to represent characters and symbols on computers and devices with support for most of the world's writing systems (including African, Arabic, Asian and Western).

Web-based Email

Web-based email provides email accounts that are accessed through a web browser. The interface is implemented as a website that provides access to various functions like reading, sending, or organizing messages.

Worm

A worm is a program or script that replicates itself and moves through a network, typically traveling by sending new copies of itself via email. Many worms have no negative effect except resource consumption, but some will perform malicious actions.

NOTE

14.4 Search Engines

The following are the some the search engine seen in web,

S.No	Name of Search Engine	Symbol of Search Engine	Description of search Engine
1.	Google	Google	**Google Search Engine is the best search engine in the world and it is also one of most popular products from Google**
2.	Bing	Bing	**It is the search engine provides different services including image, web and video search along with maps.**
3.	Yahoo	YAHOO!	**Yahoo & Bing compete more with each other than with Google**
4.	Baidu	Bai du 百度	**Baidu is the most used search engine in China and was founded in Jan, 2000 by Chinese Entrepreneur, Eric Xu. This web search is made to deliver results for website, audio files and images. It provides some other services including maps, news, cloud storage and much more.**
5.	AOL	Aol.	**Aol.com is also among the top search engines .It was named America Online in 1991 and in 2009 as AOL Inc**
6.	Ask.com	Ask .com	**Their key concept was to have search results based on a simple question + answer web format. It is a question & answer community where you can get the answers for your question and it integrates a large amount of archive data to answer your question**
7.	Excite	excite	**Excite is an online service portal that provides internet services like email, search**

			engine, news, instant messaging and weather updates
8.	DuckDuckGo		**It is a popular search engine known for protecting the privacy of the users. Unlike Ask.com they are quite open about who they use to generate search results**
9.	Wolfram Alpha	WolframAlpha	**Wolfram Alpha is a computational knowledge search engine which does not give list of documents or web pages as search results. Results are based on facts & data about that query**
10	Yandex	Yandex	**Yandex also has a great presence in Ukraine, Kazakhstan, Belarus and Turkey.**
11	Lycos	LYCOS	**Lycos has a good reputation in search engine industry. Its key areas served are email, web hosting, social networking, and entertainment websites.**
12	Chacha.com	ChaCha	Chacha.com is a human-guided search engine and was founded in 2006. You can ask anything in its search box and you will be answered in real-time. It also provides mobile search and marketing services. You can also install its mobile apps on iPhone, iPad and Android.

14.5 Chemical databases

PubChem	PubChem is a database of chemical molecules which maintains three types of information namely, substance, compound and BioAssays.

ZINC	ZINC database contains 21 million compounds available for virtual screening. In this database various molecule features like molecular weight, logP etc are included.
ChEMBL	This database provides comprehensive information about 1 million bioactive (small drug-like molecules) compounds with 8200 drug targets.
NCI	NCI database had more than 275,000 small molecules structures, a very useful resource for researchers working in the filled of cancer/AIDS.
ChemDB	It is a databse of five million chemicals which contains information of chemicals that includes predicted or experimentally determined physicochemical properties, such as 3D structure, melting temperature and solubility.
ChemSpider	ChemSpider contains more than 28 million unique chemical entities aggregated from more than 400 diverse data sources.
BindingDB	It is a binding affinity database of small molecules which contains 910,836 binding data, for 6,263 protein targets and 378,980 small molecules.
PDB-Bind	It is a collection of binding affinities for protein-ligand complexes with known three-dimensional structures. It contains 5671 protein-ligand complexes.
PDBeChem	It provides comprehensive information of ligands, small molecules and monomers. Presently it consists 15502 ligands.
KEGG	It is a database resource that integrates genomic, chemical and systemic functional information.
HMDB	A database containing detailed information about small molecule metabolites found in the human body.

SMPDB	It is Small molecule Pathway database that containing more than 350 small-molecule pathways found in humans.
BIAdb	It is a comprehensive database of benzylisoquinoline alkaloids which contains information about 846 unique benzylisoquinoline alkaloids.
DrugBank	The database that combines detailed drug (i.e. chemical, pharmacological and pharmaceutical) data with comprehensive drug target (i.e. sequence, structure, and pathway) information. The database contains 6712 drug entries including 1448 FDA-approved small molecule drugs, 131 FDA-approved biotech (protein/peptide) drugs, 85 nutraceuticals and 5080 experimental drugs.
HIT	HIT is a comprehensive database for protein targets for FDA-approved drugs as well as the promising precursors. It currently contains about 1,301 known protein targets(221 proteins are described as direct targets).
SuperNatural	A freely available database of approximately 50,000 natural compounds.
NPACT	It contains experimentally validated plant-derived natural compounds exhibiting anti-cancerous activity. Currently it contains 1574 compound entries.
TTD	This database provide information about the known and explored therapeutic protein and nucleic acid targets, the targeted disease, pathway information and the corresponding drugs directed at each of these targets.
PharmaGKB	It is a pharmacogenomics knowledge resource that encompasses clinical information of drug molecules.

NOTE

SuperDrug	This database contains approximately 2500 3D-structures of active ingredients of essential marketed drugs.

14.6 Source for List of Journals

Journal Name	Journal Impact Factor*	Citations Report
Chemical Sciences Journal	1.4 2.9 (5 Yr Journal Impact Factor)	Citations Report
Medicinal Chemistry	1.18 1.91 (5 Yr Journal Impact Factor)	Citations Report
Der Chemica Sinica	0.06 0.02 (5 Yr Journal Impact Factor)	Citations Report
International Journal of Chemical Sciences	0.6	Citations Report
Journal of Environmental Analytical Chemistry	0.35	Citations Report

Journal Name	Journal Impact Factor*	Citations Report
Research & Reviews: Journal of Chemistry	0.25	Citations Report
Trends in Green Chemistry	-	Citations Report
Inorganic Chemistry: An Indian Journal	-	-
Analytical Chemistry: An Indian Journal	-	-
Industrial Chemistry	-	Citations Report
BioChemistry: An Indian Journal	-	Citations Report

NOTE

Journal Name	Journal Impact Factor*	Citations Report
Journal of Experimental Food Chemistry	-	-
Immunochemistry & Immunopathology	-	Citations Report
Journal of Current Chemical and Pharmaceutical Sciences	-	-
RROIJ: Journal of Medicinal & Organic Chemistry	-	-
Organic Chemistry: An Indian Journal	-	Citations Report
Chemical Technology: An Indian Journal	-	Citations Report

Journal Name	Journal Impact Factor*	Citations Report
Journal of Organic & Inorganic Chemistry	-	Citations Report
Journal of Chemical Biology & Therapeutics	-	-
Journal of Neuroscience and Neuropharmacology	-	Citations Report
Scientific Reviews and Chemical Communications	-	-
Physical Chemistry: An Indian Journal	-	-
Structural Chemistry & Crystallography Communication	-	Citations Report

NOTE

Journal Name	Journal Impact Factor*	Citations Report
ChemXpress	-	-
Der Pharmacia Sinica	-	-
Chemical Informatics	-	Citations Report
Insights in Analytical Electrochemistry	-	Citations Report
Research & Reviews: Journal of Pharmacognosy and Phytochemistry	-	-

S.No	Journal Name	Journal Description	Impact Factor	Journal Abbreviation
1.	*Accounts of Chemical Research .*	It is a monthly peer-reviewed scientific journal published by the American Chemical Society containing overviews of basic research and applications in chemistry and biochemistry	Impact Factor — 22.003 (2015)	*Acc. Chem. Res.*
2.	Angewandte Chemie	It is a weekly peer-reviewed scientific journal that is published by Wiley-VCH on behalf of the German Chemical Society (Gesellschaft Deutscher Chemiker).	11.709 (2015)	Angew. Chem. Int. Ed. (English),
3.	Bulletin of the Chemical Society of Japan	It is a scientific journal published by the *Chemical Society of Japan*. It publishes accounts, articles, and short articles in the fields of theoretical and physical chemistry, analytical and inorganic chemistry, organic	2.21 (2014)	*Bull. Chem. Soc. Jpn*

		and biological chemistry, and applied and materials chemistry.		
4.	**Canadian Journal of Chemistry**	**It is a peer-reviewed scientific journal published by NRC Research Press. It was established in 1951 as the continuation of *Canadian Journal of Research, Section B: Chemical Sciences*.**	**1.003 (2015)**	***Can. J. Chem***
5.	**Chemical Communications (ChemComm)**	**It is a peer-reviewed scientific journal published by the Royal Society of Chemistry. It covers all aspects of chemistry. In January 2012, the journal moved to publishing 100 issues per year.**	**6.567 (2015)**	**Chem. Commun**
6.	**Chemical Reviews**	**It is a monthly peer-reviewed scientific journal published by the American Chemical Society.**	**37.369 (2015)**	**Chem. Rev.**

		It publishes review articles on all aspects of chemistry.		
7.	Chemistry: A European Journal	It is a peer-reviewed scientific journal that publishes articles on all areas of chemistry and related fields. It is published by Wiley-VCH on behalf of ChemPubSoc Europe.	5.771 (2015)	Chem. Eur. J
8.	Chemistry Letters	It is a peer-reviewed scientific journal published by the Chemical Society of Japan. It specializes in the rapid publication of reviews and letters on all areas of chemistry.	1.55 (2015)	Chem. Lett.
9.	Helvetica Chimica Acta	It is a scientific journal founded by the Swiss Chemical Society. It is published by John Wiley & Sons, both in print and online. It publishes papers	1.138 (2014)	Helv. Chim. Acta

NOTE

		in all areas of chemistry.		
10	**Journal of the American Chemical Society**	**It is a weekly peer-reviewed scientific journal that was established in 1879 by the American Chemical Society. The journal has absorbed two other publications in its history, the *Journal of Analytical and Applied Chemistry* (July 1893) and the *American Chemical Journal* (January 1914). It publishes original research papers in all fields of chemistry.**	**13.038 (2015)**	**J. Am. Chem. Soc**

14.7 Online Courses

National Programme on Technology Enhanced Learning (NPTEL)

The National Programme on Technology Enhanced Learning (NPTEL) was initiated by seven Indian Institutes of Technology (Bombay, Delhi, Kanpur, Kharagpur, Madras, Guwahati and Roorkee) along with the Indian Institute of Science, Bangalore in 2003. Five core disciplines were identified, namely, civil engineering, computer science and engineering, electrical engineering, electronics and communication engineering and mechanical engineering and 235 courses in web/video format were developed in this phase. The main goal of NPTEL Phase II (2009-14) was to build on the engineering and core science courses launched previously in NPTEL Phase I. An additional 600 web and video

courses were created in all major branches of engineering, physical sciences at the undergraduate and postgraduate levels and management courses at the postgraduate level. Several improvements such as indexing of all video and web courses and keyword search were implemented.

Largest online repository in the world of courses in engineering, basic sciences and selected humanities and social sciences subjects.Online web portal http://nptel.ac.in – more than 471 million+ views.Youtube channel for NPTEL – most subscribed educational channel, 1.5 million+ channel subscribers, 404 million+ views.More than 56000 hours of video content Most accessed library of peer-reviewed educational content in the world.

14.8 MOOC

Massive Open Online Courses An initiative under National Mission on Education through Information Communication Technology (NME-ICT) Programme.

The MOOCs platform will have the following facilities for the proctored exam

• Student can be prompted to register for the proctored test via a registration link available on the course Assessment page on SWAYAM platform.

• The procedures for registration for the Proctored exam can be kept simple and self-explanatory with minimum required details from student end.

• The Exam proctoring/ conducting charges and fee structure should be explained to the student in advance via the course page and introductory video.

• Provision for offline mode(s) of payment should also be kept for the students who prefer offline payment and receipt.

• Provisions for Rescheduling and Canceling the Exam should be provided to the student and Course instructor both. Proper email communication channels can be employed to immediately inform of the exam schedule changes.

A set of institutions/ Universities/ Colleges who would be part of the MOOCs initiative can also offer to proctor the exams. This can provide an option for the pan India coverage, including remote areas. Student can select his/her center from the available institutions for exam. An agency or a set of central professional proctoring agencies can be given the contract to proctor the exam for all the MOOCs offered on the SWAYAM platform.

14.9 SWAYAM

The SWAYAM covers the following

a) Curriculum based course contents covering diverse disciplines such as arts, science, commerce, performing arts, social sciences and humanities, engineering, technology, law, medicine, agriculture etc. in higher education domain (all courses to be certification-ready).

b) School education (9-12 levels) modules; for teacher training as well as teaching and learning aids to learners to help them understand the subjects better and also to help them in better preparedness for competitive examinations for admissions to professional degree programmes.

c) Skill based courses, which cover both post-higher secondary school skills that are presently the domain of polytechnics as well as industrial skills certified by the sector skill councils of various Ministries.

d) Advanced curriculum and professional certification under a unified scheme in higher education domain that can be tailored to meet the demands of Choice Based Credit System (CBCS) currently being implemented in India at under graduate level.

e) Curricula and courses that can meet the needs of life-long learners.

f) Independent courses which may not be part of any set curriculum and may be taught as awareness courses, continuing education programme and for training of specific skill sets.

14.10 Virtual Labs

The Virtual Lab is an online simulation of a chemistry lab. It is designed to help students link chemical computations with authentic laboratory chemistry. The lab allows students to select from hundreds of aqueous standard reagents and manipulate them in a manner resembling a real lab.

14.6 Check your progress questions

1. What are virtual labs?
2. Give the importance of SWAYAM module.
3. Write and explain any four terms used in emails.
4. Write a note interner service providers

14.7 Answers to check your progress questions

1. The Virtual Lab is an online simulation of a chemistry lab.
2. Curriculum based course contents covering diverse disciplines such as arts, science, commerce, performing arts, social sciences and humanities, engineering, technology, law, medicine, agriculture etc. in higher education domain. School education (9-12 levels) modules; for teacher training as well as teaching and learning aids to learners to help them understand the subjects better and also to help them in better preparedness for competitive examinations for admissions to professional degree programmes.

3. Cc

A Cc, short for "carbon copy", is a copy of an email message sent to a recipient whose email address appears in the message's Cc header field.

Email Address

An email address is a name for an electronic postbox that can receive (and send) email messages on a network (such as the internet or a local network not connected to the wider internet).

Email Body

The email body is the main part of an email message that contains the message’s text, images and other data (such as attached files).

Email Client

4. An email client is a program (on a computer or mobile device, for example) used to read and send electronic messages. Organizations consist of professional and other organizations that are either independent or nested in chemistry or education associations. Publications include both scientific magazines and academic journals. Academic journals publish articles on theoretical perspectives, laboratory practices, literature reviews, and experimental papers, including systematic evaluations of innovative practice. Conferences and Meetings include major national and international conferencesfor chemistry and chemistry education, where instructors and scholars gather annually or biannually to share experiences and communicate innovative ideas.

14.8 Summary

- Importance of using emailing services and the frequent terms employed in that communications are discussed in detail
- The various lead journals publishing research articles in chemistry are listed as table of contents.
- Online resourses for learners, teachers are discussed.
- The objectives of various online courses are accounted in this chapters

NOTE

14.9 Keywords

MOOC: Massive Open Online Courses An initiative under National Mission on Education through Information Communication Technology (NME-ICT) Programme.

NPTEL: The National Programme on Technology Enhanced Learning

Virtual lab: It is designed to help students link chemical computations with authentic laboratory chemistry.

Email Address: An email address is a name for an electronic postbox

14.10 Self Assessment Question and Exercise

1. Write a note on various on line resources available for studying chemistry.

2. Explain the objectives of NPTEL module

3. Dicuss about any four journals who are publishing scientific articles in chemistry.

4. List any four internet service providers

.

14. 11 Further Reading

1. The various online resources available in internet.

Sub. Code: 34442

ALAGAPPA UNIVERSITY
DISTANCE EDUCATION
M.Sc. DEGREE EXAMINATION
Fourth Semester
Chemistry
APPLIED CHEMISTRY
(CBCS 2018 – 2019 Academic year onwards)

Time: Three hours Maximum: 75 marks

SECTION A — (10 X 2 = 20 marks)
Answer ALL questions.

1. Name any two hazardous chemicals.
2. What are primary batteries.
3. Define corrosion
4. What is high temperature corrosion?
5. What is electroplating?
6. Give the limitations of electroless process.
7. What are nano materials?
8. How nano particles are prepared by vacuum evaporation technique?
9. How will you characterize a nano particle usind TGA?
10. Write any two terms used in emailing services.

SECTION B — (5 × 5 = 25 marks)
Answer ALL questions, choosing either (a) or (b).

11. (a) Explain the causes and consequences of ozone layer depletion.

Or

(b) Explain the method of waste water treatment by trickling filters

12. (a) Give an account on passivity.

Or

(b) Write a note on intergranular corrosion

13. (a) Discuss about the process of sacrificial anodic protection..

Or

(b) Discuss any method of surface cleaning method

14. (a) Write the advantages and limitation of electroforming process

Or

(b) Explain about spray pyrolysis process

15. (a) Write a program to calculate bond energy of chemical bond.

NOTE

Or

(b) Discuss the importance of FT-IR in the structural determination of nano particles.

SECTION C — (3 × 10 = 30 marks)

Answer any THREE questions.

16. Explain in detail about (i) Green house effect (ii) acid rain
17. Dicuss the Pourbaix diagram of Fe- H_2O system.
18. Explain in detail about the electroplating of nickel
19. Expain how SEM studies helps in the structural determination of nano particles
20. Explain the following
    a. Laser ablation process
    b. Sol-gel method
    c. concept of MOOCs